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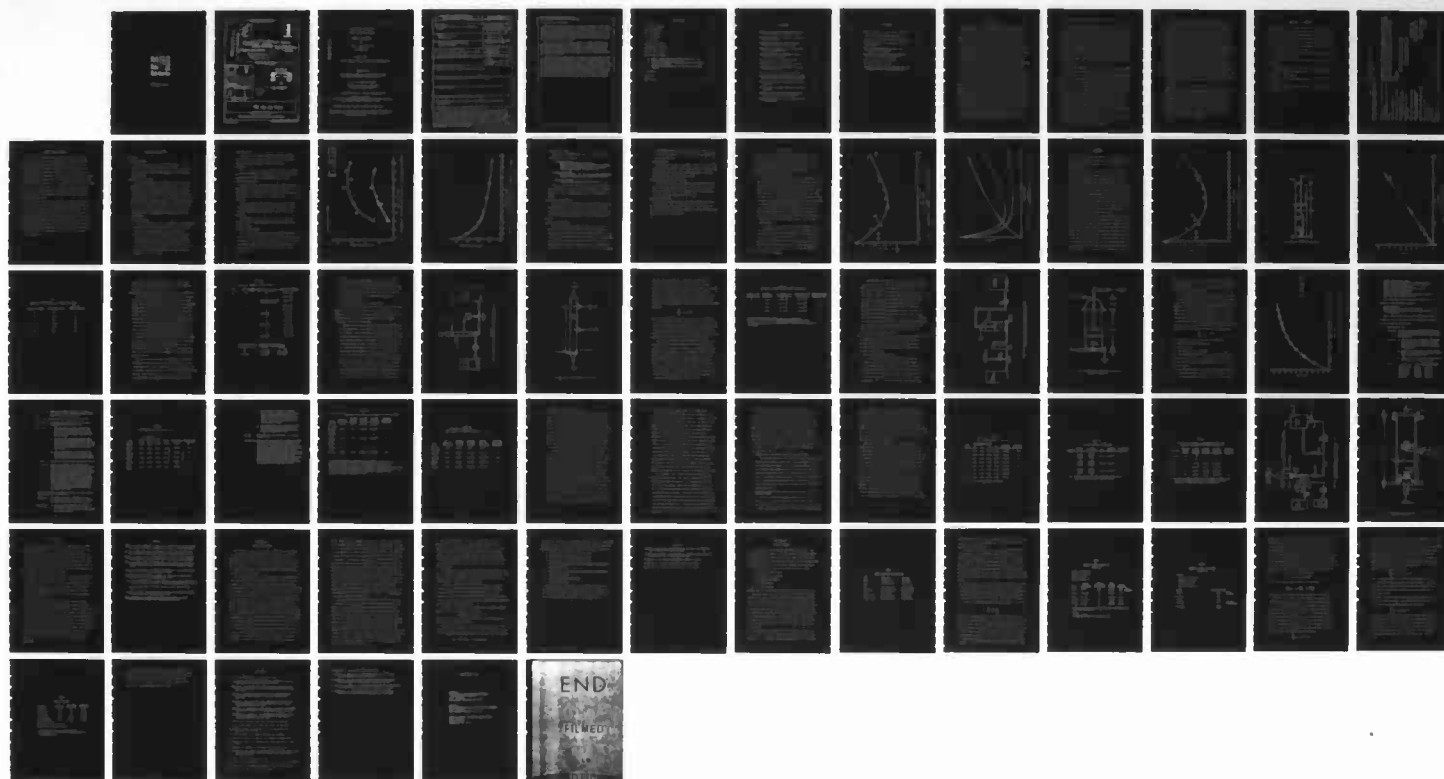
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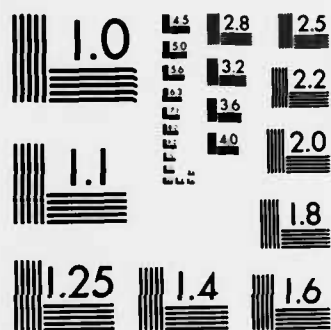
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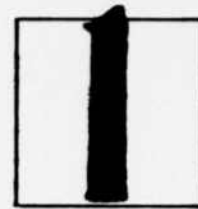
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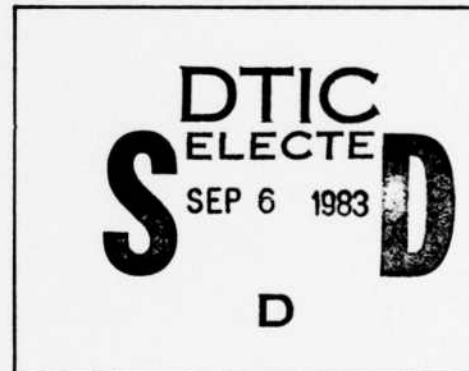
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DEVELOPMENT OF EFFICIENT
OZONE DISINFECTION SYSTEMS

FIRST ANNUAL REPORT

by

Edward S. K. Chian, Sc.D.
and
Ker Chi Chang

January 1980

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The purpose of this study was to develop an efficient ozone disinfection system based on the concept that ozone inactivation of microorganisms occurs mainly at the gas-liquid interphases. This concept has previously been confirmed on a limited extent by the author and his co-workers. A logical approach to this work was to devise systems capable of generating a larger interfacial area by either physical or chemical means. The chemical method involved the addition of surface active agents whereas the physical method involved the use		

of motionless in-line mixers.

Up to a one log-cycle improvement in ozone inactivation of E. coli was observed with the addition of 3 ppm of surface active agents in a clean water system. The most effective surface active agent was found to be a cationic detergent, Zonyl FSC, manufactured by Dupont. The use of Zonyl FSC, a fluorosurfactant, resulted in a ten-fold increase in inactivation at a 30% decrease in residual ozone concentration in clean water. Results of this study further supported the concept that ozone inactivation occurs at gas-liquid interphase rather in the bulk.

The effect of surface active agent addition on ozone disinfection was confirmed with the use of a secondary effluent. The effect of enhanced inactivation was, however, not as distinct as that obtained with a clean water system. This was due to the presence in wastewater effluent of a small amount of anionic detergent to begin with. This tended to reduce the relative effect of surface active agents addition on ozone disinfection of a wastewater effluent.

Preliminary results obtained with a mechanical system employing Lightnin and Koch motionless mixers showed that the mechanical systems were not as efficient as the ozone sparged vessel in ozone disinfection of wastewater with or without surface active agent addition. A ten-fold increase in ozone disinfection was observed by using activated carbon treated secondary effluent with the motionless mixer system. An analysis of the motionless mixer system revealed that both the hydraulic detention time and the ozone dosage were lower as compared to that employed in a sparged vessel. In addition, the complete mixing in the holding vessel of the motionless mixer system was not attained. Future work will be carried out to compare a sparged vessel vs a motionless mixer system under identical operating conditions.

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INTRODUCTION

The U. S. Army is currently pursuing upgrading their wastewater treatment facilities at Army installations, and is in serious interest in the advanced control technology to render the treated wastewater effluent unharmed to the environment. Ozone disinfection would therefore provide the way to pollution control with minimum impact to the environment.

This interest in ozone has been generated by the recent concern about the widespread use of chlorine as a wastewater disinfectant. The presence of certain chlorinated compounds and the potential toxicity of these compounds to aquatic environments have been well documented; several investigations have implicated chlorination of wastewater effluents in the creation of carcinogenic compounds found in the water supplies of many cities. Ozonation of wastewater will potentially alleviate both of these adverse effects.

The cost of ozone is, however, felt to be much greater than that of chlorine for wastewater disinfection. This has accounted for ozone's limited use to date. For example, Ghan et al. (1976) have reported an ozone dosage of 10 mg/l is necessary for meeting a disinfection criterion of total coliform equal to or less than 2.2/100 ml with secondary effluent containing low concentrations (e.g., a few ppm) of color-bearing materials, suspended solids, turbidity and COD; while an effluent with high concentrations (e.g. tens of ppm) of these substances requires ozone dosages in excess of 50 mg/l to meet the same bacteriological quality. The cost of disinfecting secondary effluent with ozone could therefore be more than 10¢/1000 gal in the latter case based on the state-of-the-art ozone generation from oxygen. This is high compared to the total cost of approximately 15-20¢/1000 gal for secondary treatment of wastewater. McCarty and Smith (1974) have compiled a comprehensive list of ozone dosages and contact times mainly for disinfection of various

types of waters and wastewaters which fall in the same range of ozone dosages.

It has been shown by Farooq and his coworkers (1976, 1977) that ozone residual is one of the controlling factors in inactivating microorganisms. Following the initial appearance of an ozone residual in the effluent, rapid inactivation of microorganisms occurred in the first few seconds regardless of the type of water used, i.e., clean water and secondary wastewater effluent. The level of ozone residual required to accomplish such rapid inactivation of microorganisms, commonly known as the "all or none" type of inactivation mechanism, is on the order of a few tenths of one mg/l. However, a significant amount of ozone dosage is needed to achieve the same level of ozone residual in the treated wastewater effluent as compared to that needed in the clean water.

An alternative approach to achieve an adequate level of ozone residual for disinfection is to take advantage of the existence of a higher concentration of dissolved ozone at the gas-liquid interface and in the stagnant liquid film surrounding the gas bubbles - a concept commonly recognized by chemical engineers. Generally the thickness of this liquid film is on the order of 75 to 100 μ ($1 \mu = 10^{-4}$ cm), whereas the size of bacteria and yeasts is approximately 1 μ and 10 μ in diameter, respectively. Even with an aqueous layer of water ($\sim 20 \text{ \AA}$ in thickness) normally bound to the microorganism as an integral part of the cell wall, the size of microorganisms is still much smaller than the thickness of the liquid film. Therefore, it is likely that these organisms can be transported into the liquid film through convective and diffusional means and thus exposed to an ozone residual higher than that measured in the bulk. Higher efficiency of ozone disinfection has indeed been observed by Farooq (1976) in the presence of ozone gas bubbles at the same level of residual ozone. An increase of one and one-half log cycles of inactivation of yeasts was reported (Farooq, 1976).

The importance of ozone gas bubbles in disinfection has also been recognized by other researchers. Rosen et al. (1974) designed an ozone contact chamber based on the assumption that inactivation results when the microorganism comes into contact with an ozone bubble regardless of the ozone concentration in the bulk solution. Hill and Spencer (1974) reported that the inactivation reaction takes place near the surface of the bubble as free suspended bacteria migrate to the interface due to their surface active properties. Masschelein et al. (1975) also emphasized the importance of contact between an "ozone bubble" and microorganisms. Therefore, it is speculated that the rate of disinfection may not be limited by the action of residual ozone alone as described previously. If the phenomenon of transporting microorganisms to the gas-liquid interface through the surface active properties of cell wall or with the aid of surface active agents is analyzed in light of the findings of Farooq (1976), it may be visualized that any process modification which would assist microorganisms to migrate to the gas-liquid interface would be beneficial in that the microorganisms would be exposed to a higher concentration of dissolved ozone existing in the liquid film.

Based on the above concept, an improvement of contact between the microorganisms and the gas-liquid interface can be made by employing various gas-liquid contactors known to generate intimate gas-liquid contact, and by evaluating surface activate materials that will facilitate transport of microorganisms to gas-liquid interface. The criteria of selecting such surface active materials are that they should be inert to ozone degradation, especially being inert within a period of time the disinfection process occurring, and they should not be required in quantities to the extent of being detrimental to the effluent quality.

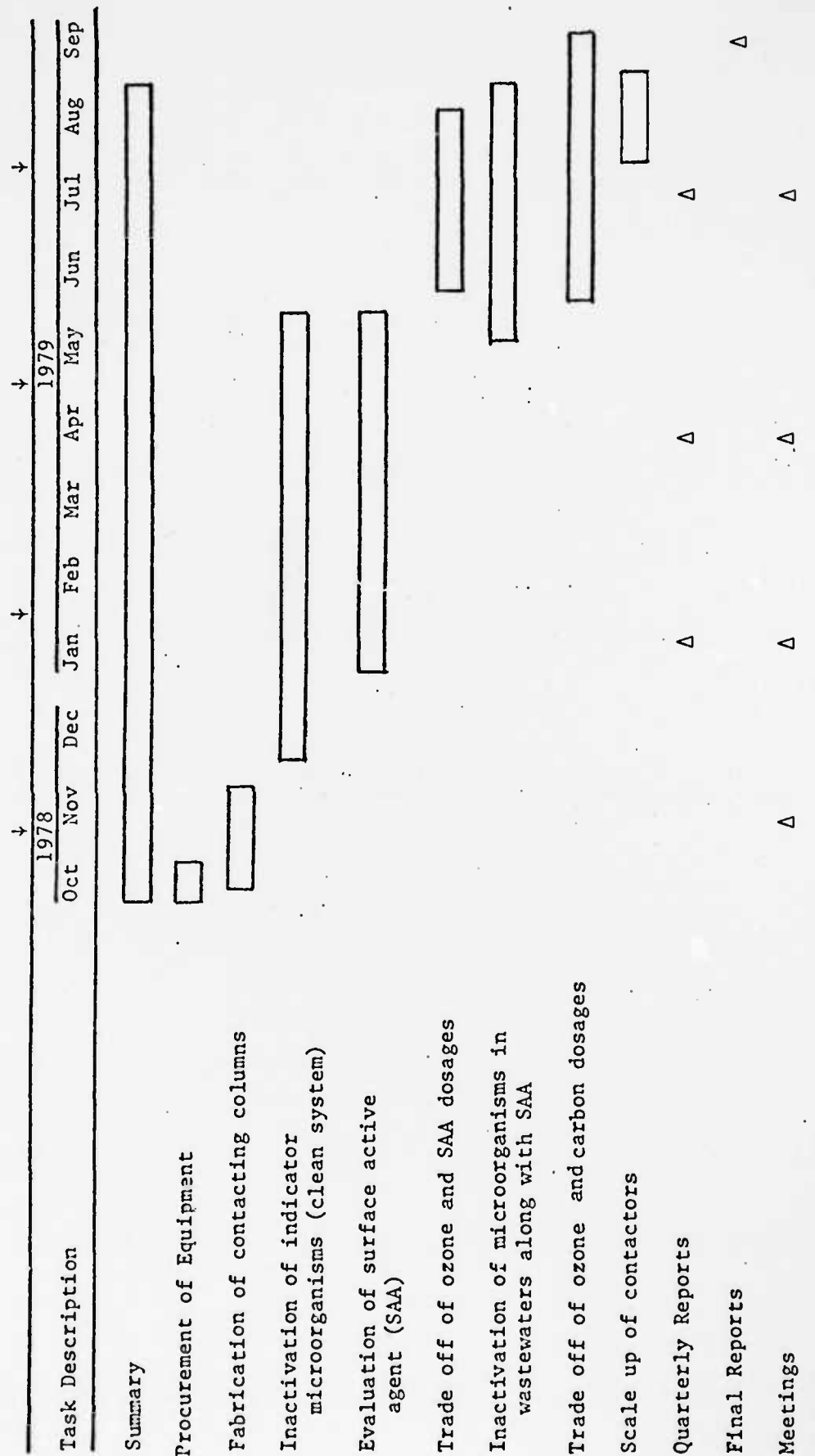
OBJECTIVE OF RESEARCH

The purpose of this study was to develop means of improving the efficiency of ozone disinfection in relation to ozone consumption so that a viable process can emerge from ozone disinfection of wastewater. The major objectives of this research work were to implement findings of Farooq and his co-workers (1976, 1977) on some of the parameters that govern the efficiency of ozone inactivation of microorganisms. The specific parameters under this study are given in the following:

1. Enhancement of gas-liquid contact using various surface active agents at several levels.
2. Generation of large gas-liquid interface using various motionless in-line mixers.
3. Effect of wastewater on ozone inactivation of microorganisms.
4. Effect of activated carbon treatment of wastewater on ozone inactivation of microorganisms.
5. Effect of gas phase ozone concentration on inactivation of microorganisms.

A graphical schedule showing the duration, sequence and time of major tasks is given in Chart 1.

Project: Development of Efficient Ozone Disinfection System
Principal Investigator: Edward S. K. Chian.



EXPERIMENTAL PROCEDURES

Effective contacting of ozone gas with microorganisms to promote inactivation is believed to be an important part of an ozone disinfection system according to Farooq, Chian and Engelbrecht (1977). This can be accomplished by means of either increasing the interfacial area of ozone gas-liquid contact or enhancing the migration of microorganisms from the bulk to the gas-liquid interphase. The former can be realized by generating a large gas-liquid interfacial area with a mechanical process, such as the use of a mixer or a motionless mixer, or a chemical process, such as the application of surface active agents (SAA) to reduce the surface tension of water. The latter can be realized by adding SAA to improve the surface active properties of microorganisms and thus enhances their migration to the gas-liquid interphase.

This study was carried out in four phases. In phase I of this study, the effect of surface active agents (SAA) on ozone inactivation of E. coli was determined in a batch reactor using tap water (clean system). The same experiments were carried out in Phase II of this study using a continuously flow reactor. The effect of different SAA on ozone inactivation of E. coli in a clean system was studied in Phase III and the results were compared with that with a secondary effluent. In the last phase of this study, the effect of gas-liquid interface generated by various motionless in-line mixers on ozone inactivation of microorganisms was studied with the secondary effluent.

MATERIALS AND METHODS

A. Materials

1. Model Organisms:

Escherichia coli was used as the model organisms in this study. The selection of E. coli was that coliform organisms are normally used as an indicator microorganism in water and wastewater treatment.

2. Preparation of E. coli

The culture was grown in E. C. broth for 24 hr at 44.5°C in a temperature controlled incubator (Despatch Oven Co., Style D0-7 Serial #50194). Cells were harvested by means of a centrifuge (Chicago Surgical & Electrical Co., Cat. #20R, Model #61, Serial #1421) at 1800 rpm for 15 min. Pour out supernatant and fill with phosphate buffer. Resuspend the culture by a mixer (Vortex-Genie Sci. In., Cat. #12-812-VI, Serial #FG). Repeat the previous two procedures. The final E. coli were kept at 4°C until needed. A cell concentration of approximately 10^8 /100 ml was used in the experiments.

3. Medium Preparation

- a. E. C. broth: Dissolve 37 g of E. C. medium in 1 l of distilled water. After sterilized by autoclave for 15 min, cool down and store in the refrigerator. The pH should be 6.9.
- b. M-FC broth: Dissolve 3.7 g of M-FC broth in 100 ml of distilled water. Add 1 ml of 1% rosolic acid in 0.2 N NaOH. Heat the medium to the boiling point, promptly remove from heat and cool to below 45°C. The final pH is 7.4. The finished media is stored in the refrigerator at 4°C and any unused medium discarded after 95 hr.

4. Phosphate Buffer

Dissolve 1.7 g of potassium dihydrogen phosphate (KH_2PO_4) and 0.3 g of sodium hydroxide (NaOH) in 5 l of deionized (DI) water, giving a strength of 0.0025 M. The pH was around 7.

5. Tap Water

Open the faucet let water run for 30 min then fill in a glass bottle. Store overnight to dechlorinate it and to allow the water temperature equilibrated to room temperature, i.e., 25°C.

6. Ozone Demand Free Water

Distilled DI water was ozonated for 15 min to remove any ozone oxidizable trace organic matter and then boiled to dissipate the ozone residue. To further ensure the dissipation of any ozone residue, the water was kept overnight under ultraviolet light.

7. Glassware

All glassware used in the experiments was cleaned by soaking overnight followed by rinsing in tap water and DI water. Sterilization was accomplished in an autoclave at 121°C, 15 psig for 1 hr.

8. Wastewater

The wastewater effluent used in this study, was secondary effluent obtained from the Clayton Water Pollution Control Plant, Atlanta, Georgia.

9. Air/Ozone or Oxygen/Ozone

Air (or oxygen) from the pressurized gas cylinder was passed through a tube filled with fiberglass wool then fed to a Welsbach 816 ozone generator. The ozonator was operated at a pressure of 8 psig and a voltage setting of 50-70 volt. The ozone concentration in the gas phase under different operating conditions are given in Figures 1 and 2.

Ozone Concentration vs. Voltage

- : Q = 0.2 l/min. O₂ generated
 □: Q = 0.2 l/min. Air generated
 △: Q = 0.5 l/min. O₂ generated

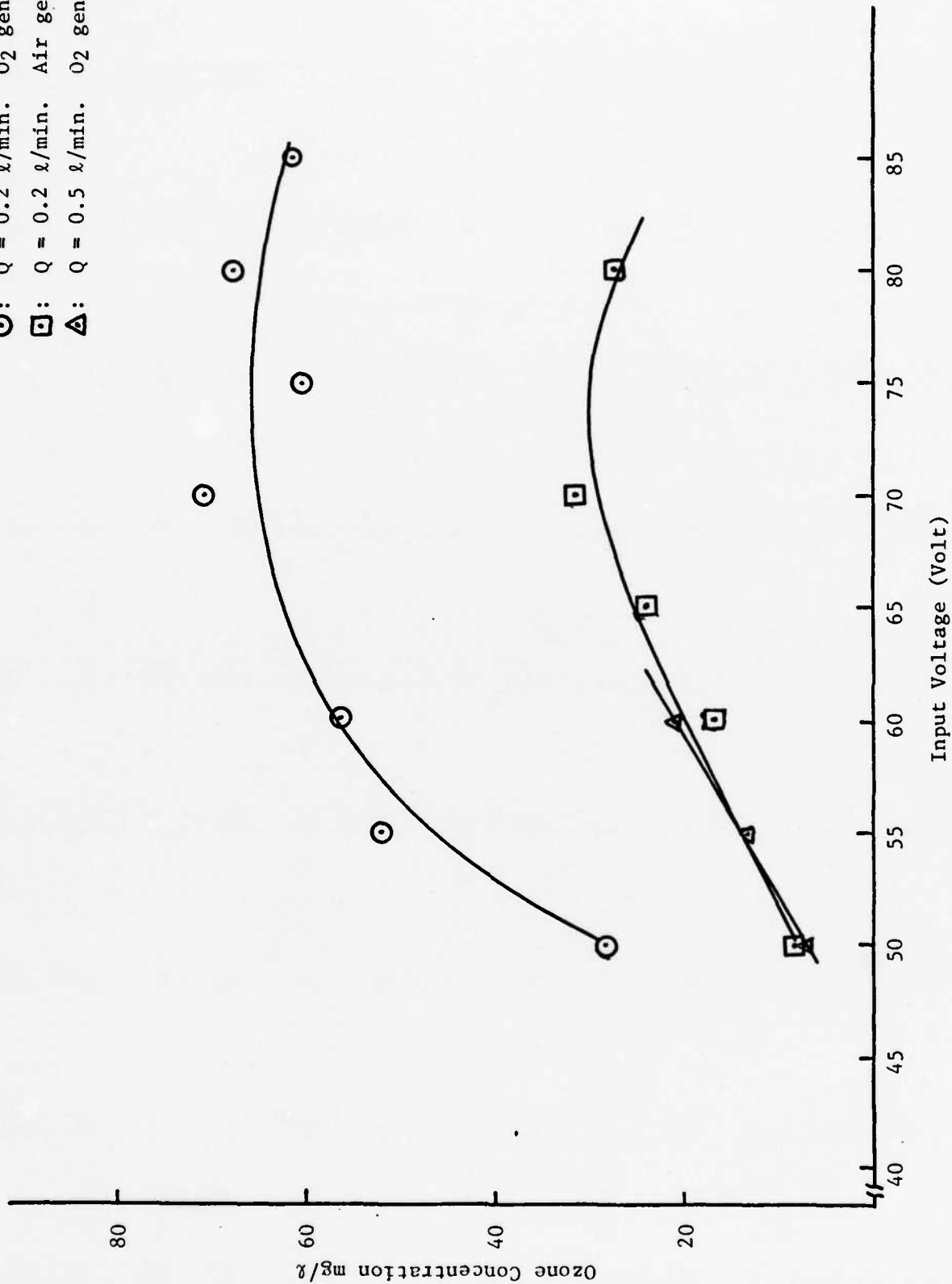


Figure 1. Calibration curve for gas phase ozone concentration vs input voltage of the Welsbach T-816

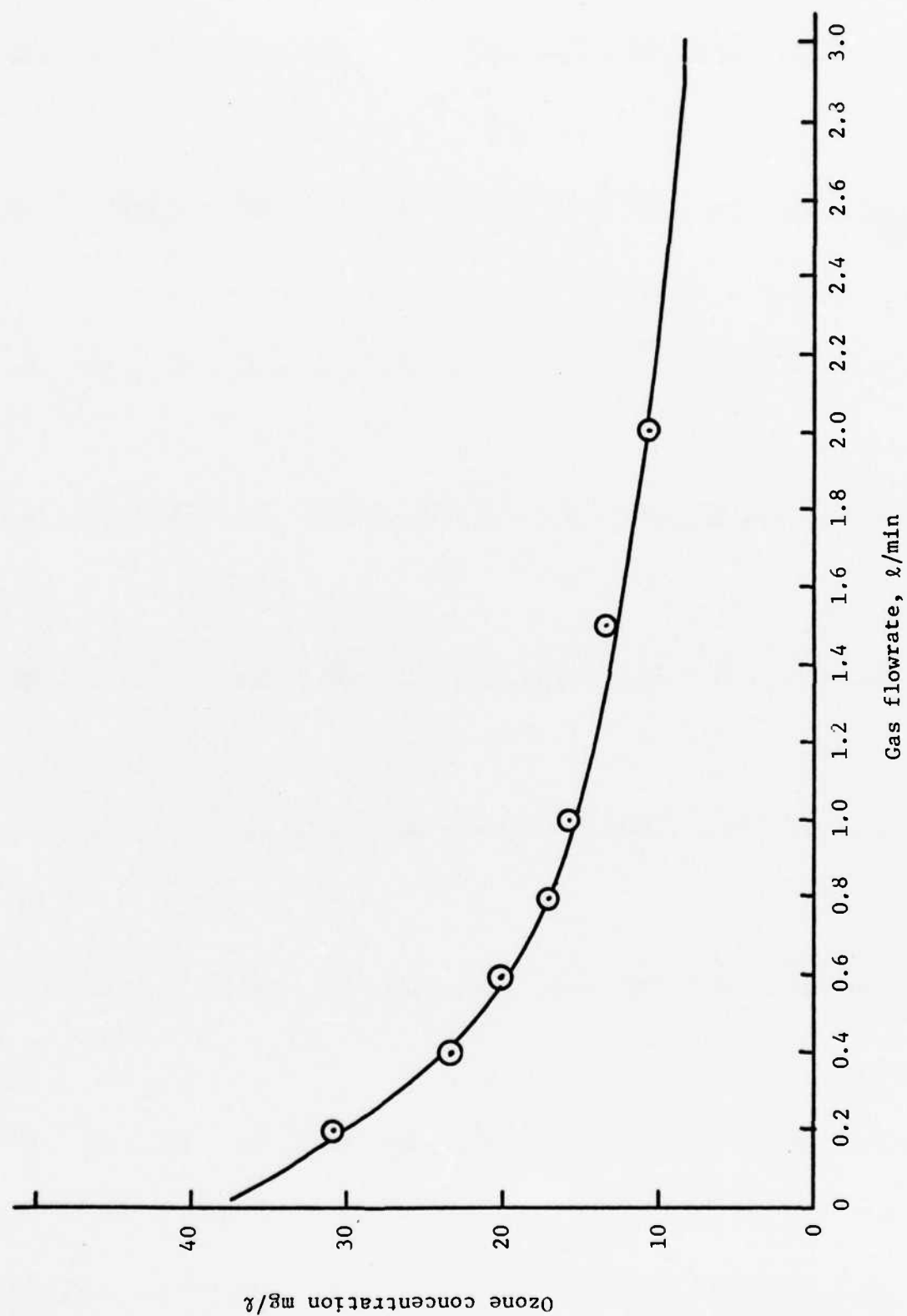


Figure 2. Ozone concentration vs. flowrate @ 70 volt generated from pure oxygen

10. Surface Active Agents

Three types of detergents were purchased and some of them were examined in this research:

a. Anionic Detergent:

UCANE 12, Union Carbide Co. LAS (C₁₂)
Alkanol 189-S, DuPont (Sodium hydrocarbon sulfonate)
Alkanol DW, DuPont (Sodium alkylaryl sulfonate)
*Sodium Lauryl Sulfate, Aldrich Chem. Co.

b. Nonionic Detergent:

*Brij 35, ICI U.S. Inc. (Polyoxyethylene Lauryl Ether)
Triton X-405, Rohn & Haas Co. (Polyethoxy ethanol)

c. Cationic Detergent:

*Cetyltrimethyl Ammonium Bromide, Aldrich Chem. Co.

Since the use of surface active agents constitutes the major task in this study, a literature review on surfactants is given in Appendix I to aid in understanding the principles involved in their usage.

11. Motionless In-Line Mixers

Upon a survey of the literature on the motionless in-line mixers (see Appendix II), a 5" x 1" Koch mixer and a 16" x 1" Lightnin inliner were purchased for this study. The engineering principles behind the use of motionless mixers are also given in Appendix II.

B. Methods

1. Enumeration Techniques

1 ml of 0.005 N Na₂S₂O₃ · 5H₂O was added to a 10-ml test tube before collecting the E. coli sample so that the residual ozone in the sample can be eliminated. Dilute the sample with phosphate buffer to an appropriate level so that it will yield from 20 to 80 coliform colonies. Total colony count should not exceed 200. After the diluted sample was filtered, the Millipore filter was transferred to a plastic petri dish (50 x 9 mm with tight lid, Falcon) containing

a sterile absorbent pad saturated with 2 ml of M-FC medium. Invert the dish and incubate for 24 hr in a 44.5°C incubator. Examine and count all blue colonies.

2. Ozone Residuals

Equal amounts of sample and potassium iodide (KI) solution (2%) were added in a test tube. Store in dark for 30 min. The dissolved ozone concentration was determined using a Beckman-26 U-VIS-IR spectrophotometer at 352 nm (Shechter, 1973).

3. Concentration of Ozone in Gas Phase

Pass ozone gas through a gas washing bottle containing 200 ml of 2% KI solution. Then add 10 ml of 1.0 N H_2SO_4 to lower the pH below 2.0. Titrate with 0.005 N $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ to the end point.

For 0.005 N $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, 1 ml = 0.12 mg O_3 .

C. Ozone Contactor Systems

Several different reactor designs and feeding systems were fabricated and evaluated during various phases of this study. These systems can best be discussed under each phase of studies in order to eliminate possible confusion that might be encountered.

RESULTS AND DISCUSSION

A. Phase I Batch Study with Surface Active Agents (SAA) in a Clean System

Batch studies on the effect of a non-ionic surfactant, Brij 35, on the mass transfer coefficient, $k_L a$, of oxygen and the ozone inactivation of E. coli were carried out in this phase of the study. The results of these experiments are discussed in the following.

1. Preliminary Evaluation of Surfactants

The effect of Brij 35 surfactant on the mass transfer rate dc/dt of ozone in water was studied (Fig. 3). In principle the addition of surfactants will increase the interfacial area, "a", area per unit volume, as a result of a decrease in surface tension of water. However, the overall liquid film mass transfer coefficient, k_L , tends to decrease resulting from forming a rigid film by the surface active materials at the gas-liquid interphase. This rigid film will increase the resistance for gas molecules diffusing across the interface. Since a faster increase in "a" and a slower decrease in " k_L " were found at higher concentrations of SAA addition, the product of $k_L a$ will reach a minimum at a given SAA concentration, then increases to higher values at higher SAA concentrations. Figure 4 depicts such a relationship.

The volumetric mass transfer rates of ozone based on triplicate runs are plotted in Figure 3. The ordinate is expressed in dissolved ozone concentration in ppm determined after five seconds, thus it represents the volumetric ozone transfer rate, dc/dt . Since the equilibrium concentration of ozone, C^* , at a gas phase ozone concentration of 16.6 mg/l employed in this study is approximately 3.3 mg/l, the mass transfer coefficient can be calculated according to the following relationship

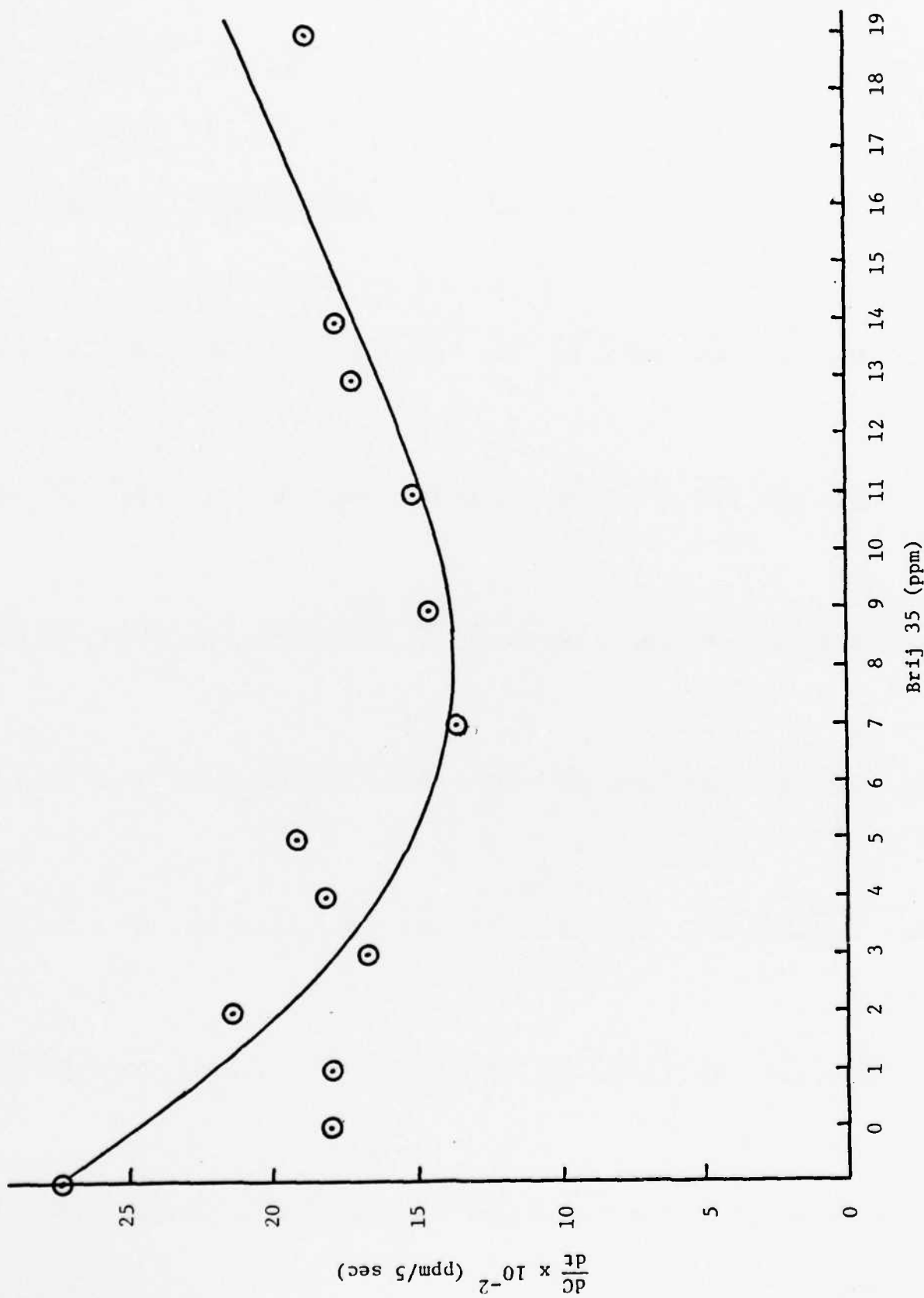
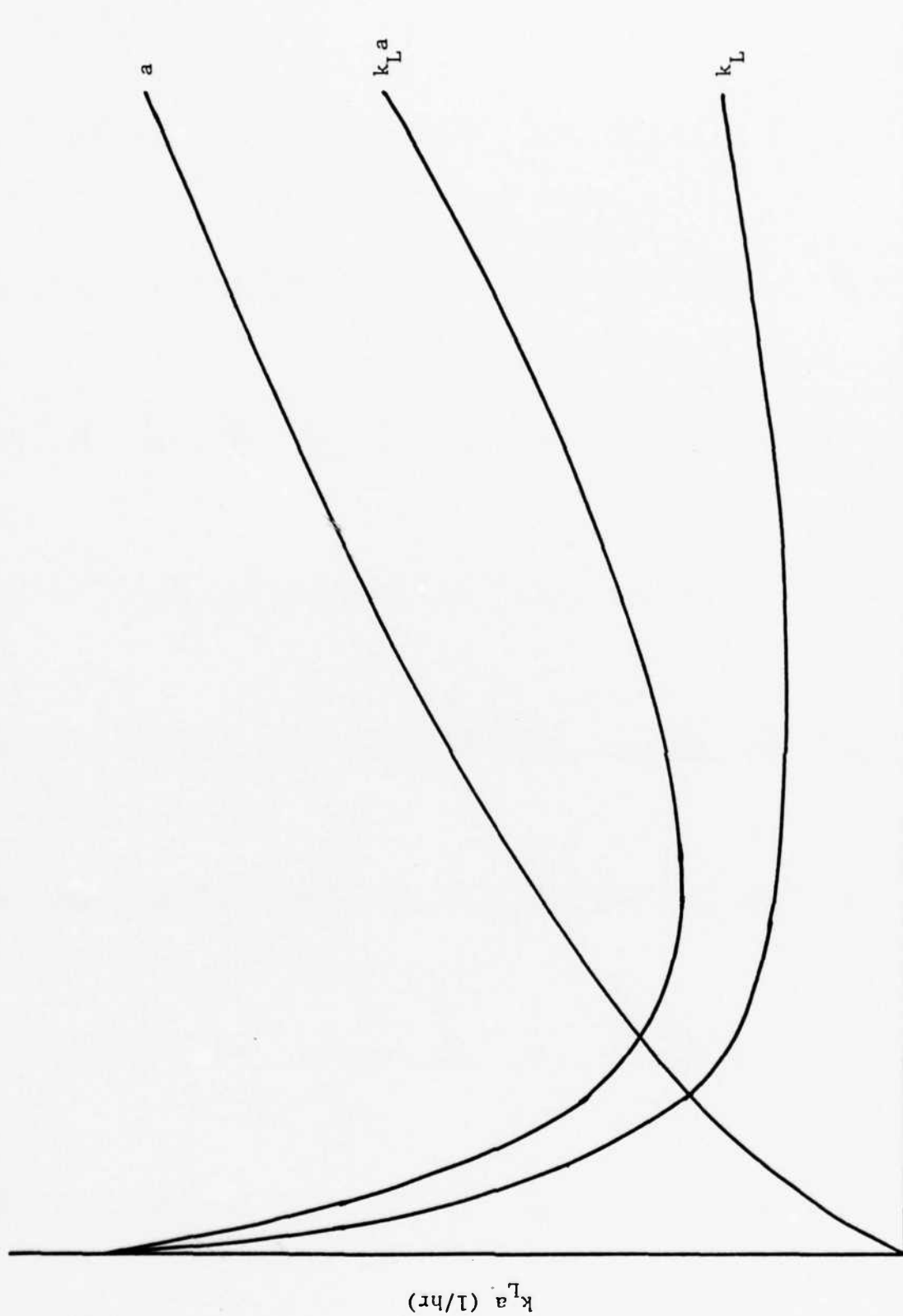


Figure 3
Volumetric Mass Transfer Rates of Ozone vs. Concentration of Brij 35 Surfactant



C_S (ppm), NaLSO_4

Figure 4

$k_L a$, a and k_L of Oxygen vs. Concentration Sodium Lauryl Sulfate Surfactant

$$k_L a = \frac{dc/dt}{(C^* - C)}$$

where C is given in Figure 3 at various surfactant addition. A plot of ($k_L a$) versus Brij 35 surfactant in ppm is given in Figure 5. A minimum of $k_L a$ is also observed in Figure 5 as that predicted from Figure 4.

These experiments were carried out in a cylindrical glass vessel having an internal diameter of 4.5 cm and a liquid height of 11.5 cm (approximately 200 ml of water, Figure 6). Ozone was generated with a Welsbach Model T-816 laboratory ozonator using cylindrical oxygen as feed gas. The gas phase ozone concentration was 16.6 mg/l (or 0.77% by volume) as determined according to procedures outlined in Standard Methods (1975). Ozone was introduced through a 2-cm diameter fritted glass disc at a flow rate of 1 liter/min. The dissolved ozone concentration was determined using the method reported by Schechter (1973). Figure 7 gives the calibration curve of dissolved ozone concentration versus absorbance at 352 nm using a Beckman-26 UV-VIS-IR Spectrophotometer.

The amount of Brij 35 surfactant to be employed should be at a level where the dissolved ozone concentration is a minimum. This represents a minimum amount of ozone required. However, in practice, the amount of SAA employed may be less than that given a minimum ozone concentration. This is dependent upon the amount of foam formed, and the level of detergent permissible from the stand points of both its costs, and health and ecological effects. Table 1 gives the height of foam formed, along with its average percentage to the initial liquid volume, at various concentrations of SAA addition after 5 seconds of ozone sparging. In a conventional reactor design

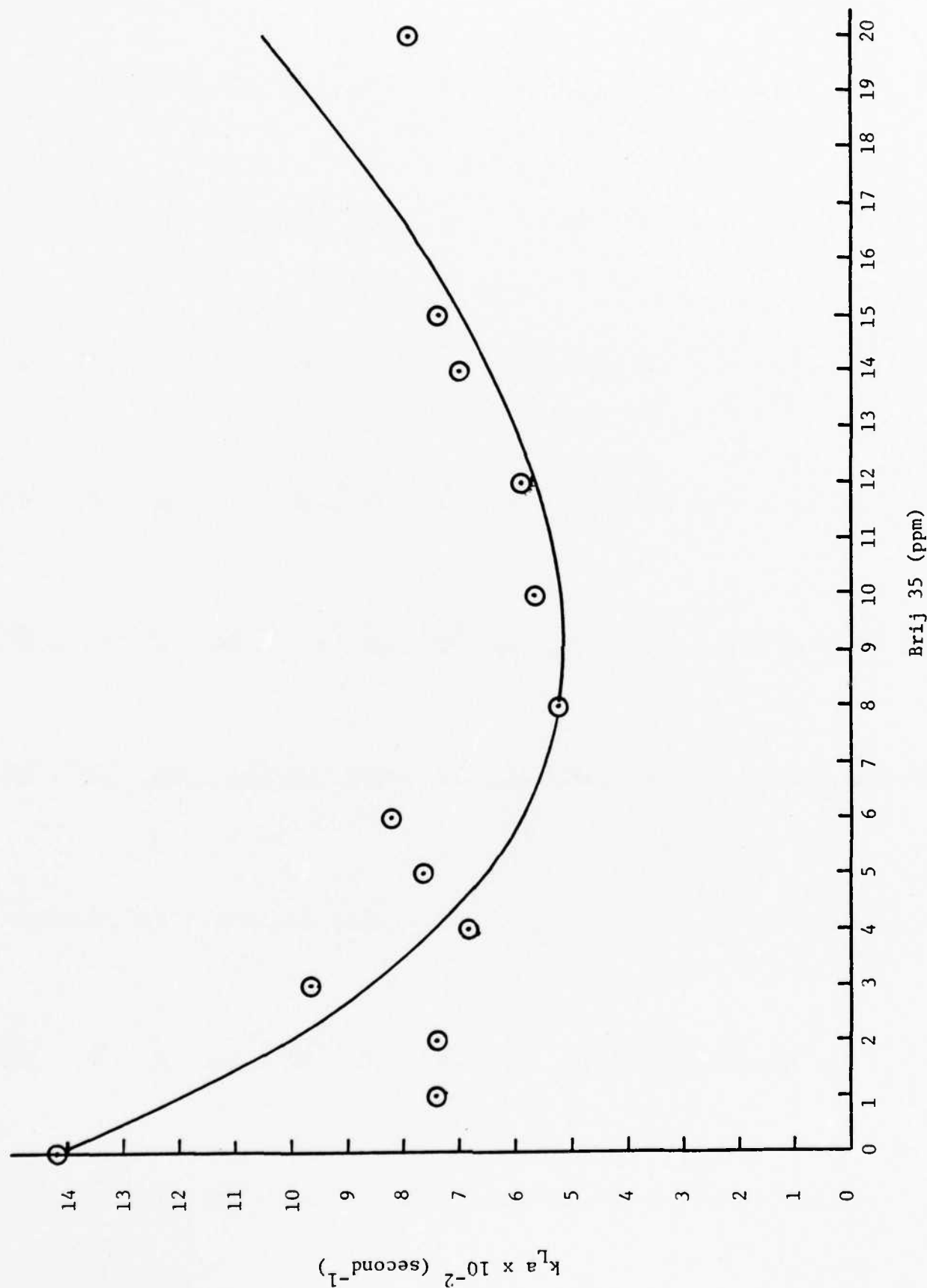


Figure 5
Overall Mass Transfer Coefficient of Ozone vs. Concentration of Brij 35

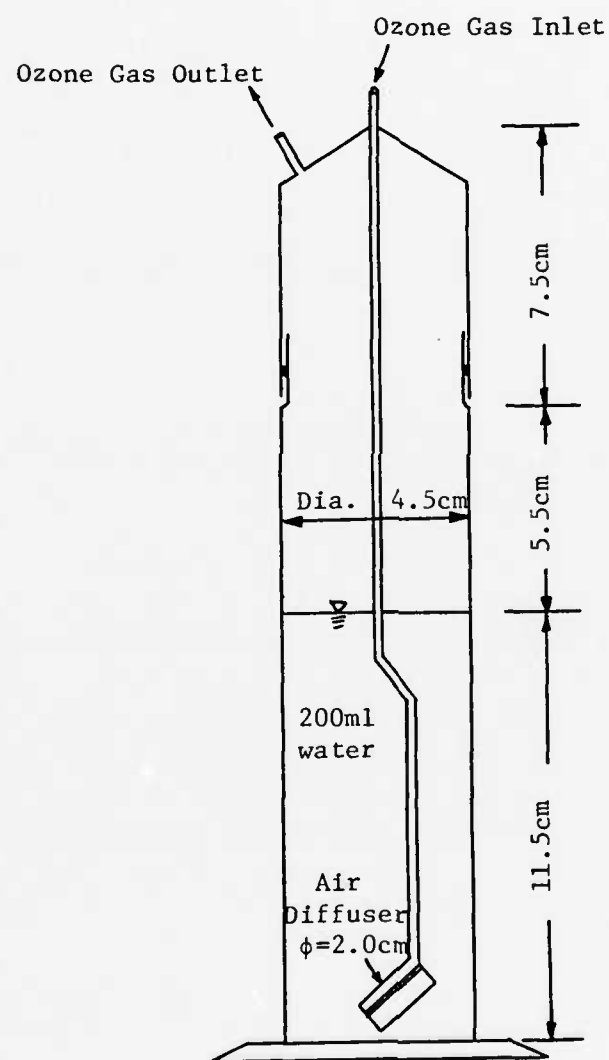


Figure 6
Ozone Contactor for Disinfection Studies

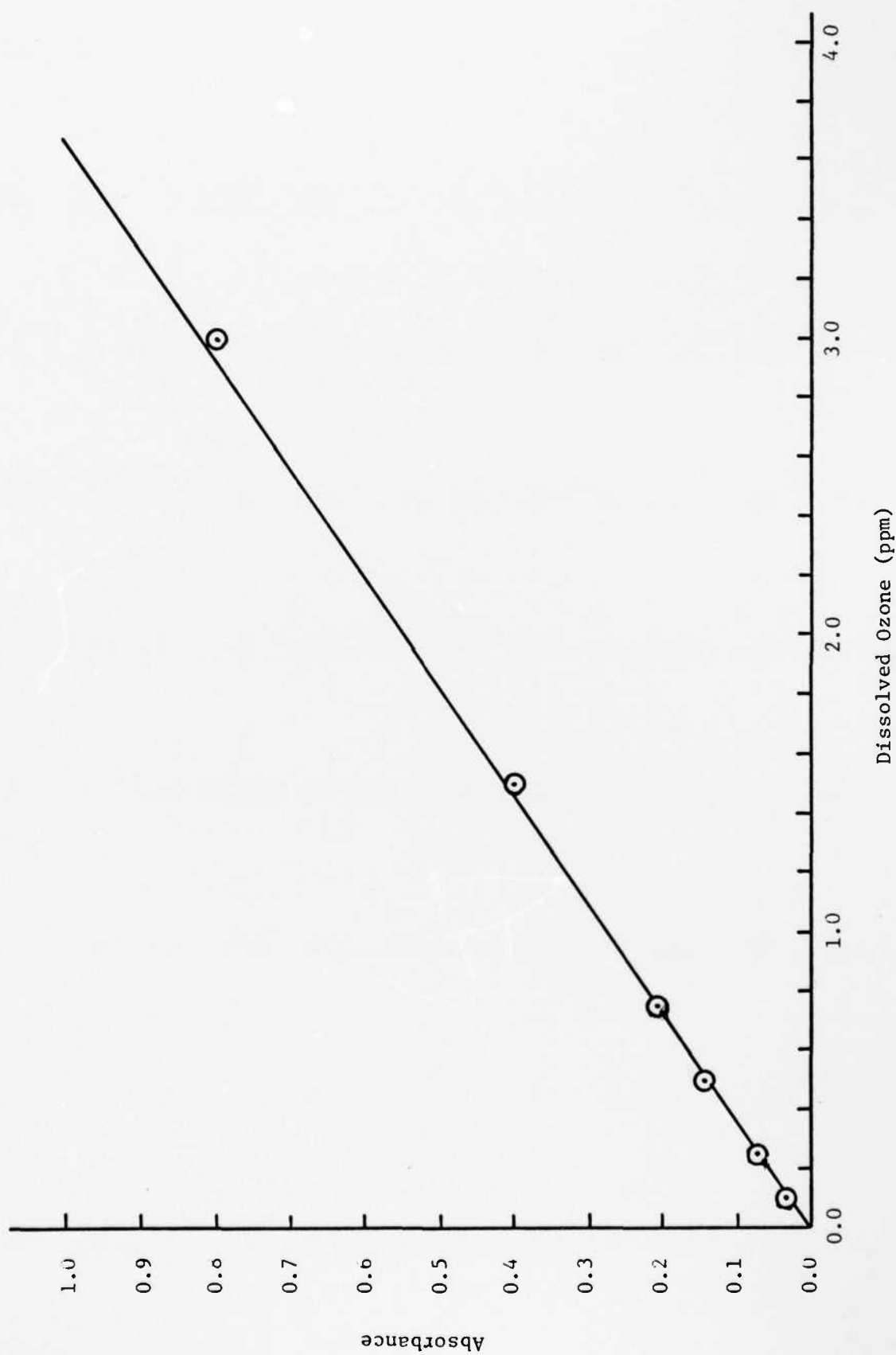


Figure 7
Calibration Curve of Ozone Measured at 352 nm

Table 1

Formation of Foam versus Brij 35 Addition to Water

SAA Brij 35 (ppm)	Foam Height (cm)	Avg % of Volume Expansion
0	0	0
3	1-2	13
5	2-3	22
6	3-35	28
8	4-5	39
10	5-6	48

a freeboard volume of 20% is normally provided. Therefore an addition of 3 ppm Brij 35 was selected in the later experiments on inactivation of microorganisms by ozone.

2. Preliminary Studies on the Effect of Surfactant on Ozone Disinfection

A one-day old pure culture of coliforms diluted to a concentration between 10^7 to 10^9 per 100 ml of water was employed in this study. The Millipore membrane filter method as outlined in Standard Methods (1975) was used to enumerate coliforms. The ozone disinfection conditions were identical to those employed in detergent studies. A series of 11 runs, i.e., 5 with SAA addition at 3 ppm and 6 without, was made. The latter were used as a control. Preliminary results showed a four to five log-cycle reduction in coliforms after 5 seconds of ozonation in ozone-demand-free water. However, no survival of coliforms was observed (i.e., greater than 6 log cycles of inactivation) after 10 seconds of ozonation. With the addition of 3 ppm Brij 35, an approximate of three-fold increase in inactivation of coliforms was observed. The average percentage of survival was 1.3×10^{-3} with 3 ppm Brij 35 addition, and 3.7×10^{-3} without SAA. The variation in cell enumeration procedures was found to be less than 20% from the average including enumerating at different dilutions.

In order to determine whether the enhancement in inactivation with detergent addition (3 ppm) is due either to lysis of cells or to foam separation, a set of control experiments was conducted with air sparging. These involve duplicate runs with and without detergent addition. Table 2 shows that there are no effects in foaming on cell enumeration with or without detergent addition at 3 ppm level.

Table 2

Effect of Foaming on Coliform Enumeration

<u>Run</u>	<u>Brij 35 (ppm)</u>	<u>Time of Aeration, min</u>	<u>Coliforms #/100 ml</u>
A1	0	0	7.6×10^8
		5	7.3×10^8
		w/o Foam (i.e. after foam disappeared)	6.5×10^8
A2	0	0	6.0×10^8
		5	6.0×10^8
		w/o Foam	5.6×10^8
B1	3	0	4.7×10^8
		5	5.4×10^8
		w/o Foam	6.5×10^8
B2	3	0	5.5×10^8
		5	4.6×10^8
		w/o Foam	4.0×10^8

<u>Time after aeration min</u>	<u>Average #Coliforms/100 ml</u>	
	<u>A1/A2</u>	<u>B2/B1</u>
0	6.8×10^8	5.1×10^8
5	6.7×10^8	5.0×10^8
w/o foam	6.1×10^8	5.2×10^8

The average coliform concentrations between runs A1 and A2 and runs B1 and B2 themselves are essentially identical with or without aeration, i.e., 5 min vs zero min aeration. The slight differences between runs A (without SAA) and B (with 3 ppm SAA) is, however, within the reproducibility of the enumerating procedures, i.e., within 20% from the average.

B. Phase II Continuous Runs with SAA in a Clean System

The efforts made in this phase of the study have been directed toward verification of the effect of surface active agent addition on ozone disinfection in a clean system using a continuously flow reactor. The experimental procedures and results are given in the following.

1. Design of Ozone Contacting Systems

Based on the encouraging results obtained with a batch system on ozone inactivation of microorganisms in the presence of surface active agents, a continuously flow, well-mixed reactor was fabricated to further substantiate the results of preliminary studies. Figure 8 shows a schematic diagram of this system. The reactor employed in this study was made of Pyrex. It has an internal diameter of 3.0 cm and a maximum liquid height of 21 cm which gives a liquid volume of approximately 160 ml (Figure 9). Ozone gas was introduced at the bottom of the reactor through a fritted glass diffuser. Influent of inoculated water was fed to the reactor at the bottom, whereas the effluents can be withdrawn from either one of the ports at the top.

In order to assess the mixing of microorganisms in the reactor under the prevailing ozonation conditions, tracer studies were made. This was done by feeding a colored solution (bernachrome blue dye) at a flow rate of 960 ml/min into the ozone sparged reactor after it

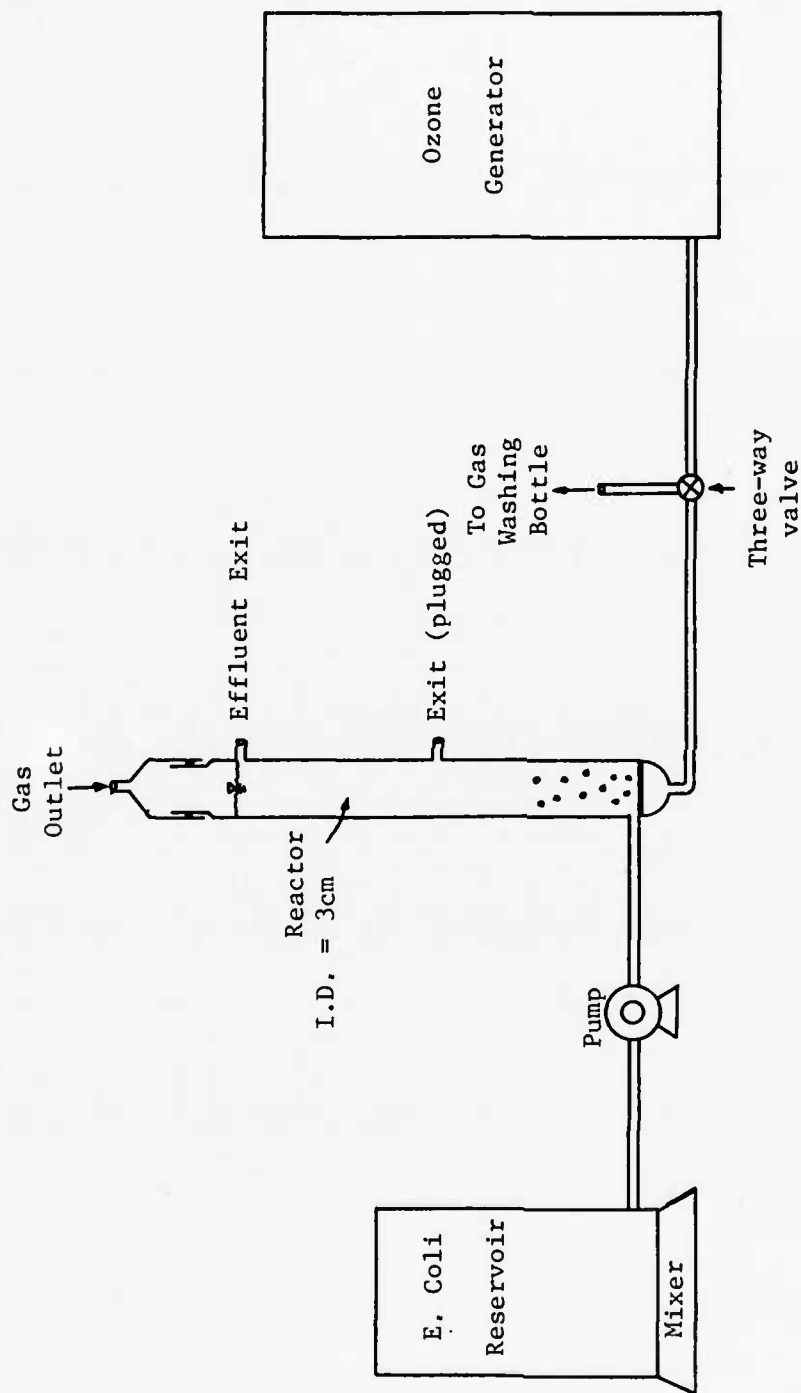


Figure 8
Schematic diagram of a continuously flow ozone disinfection system

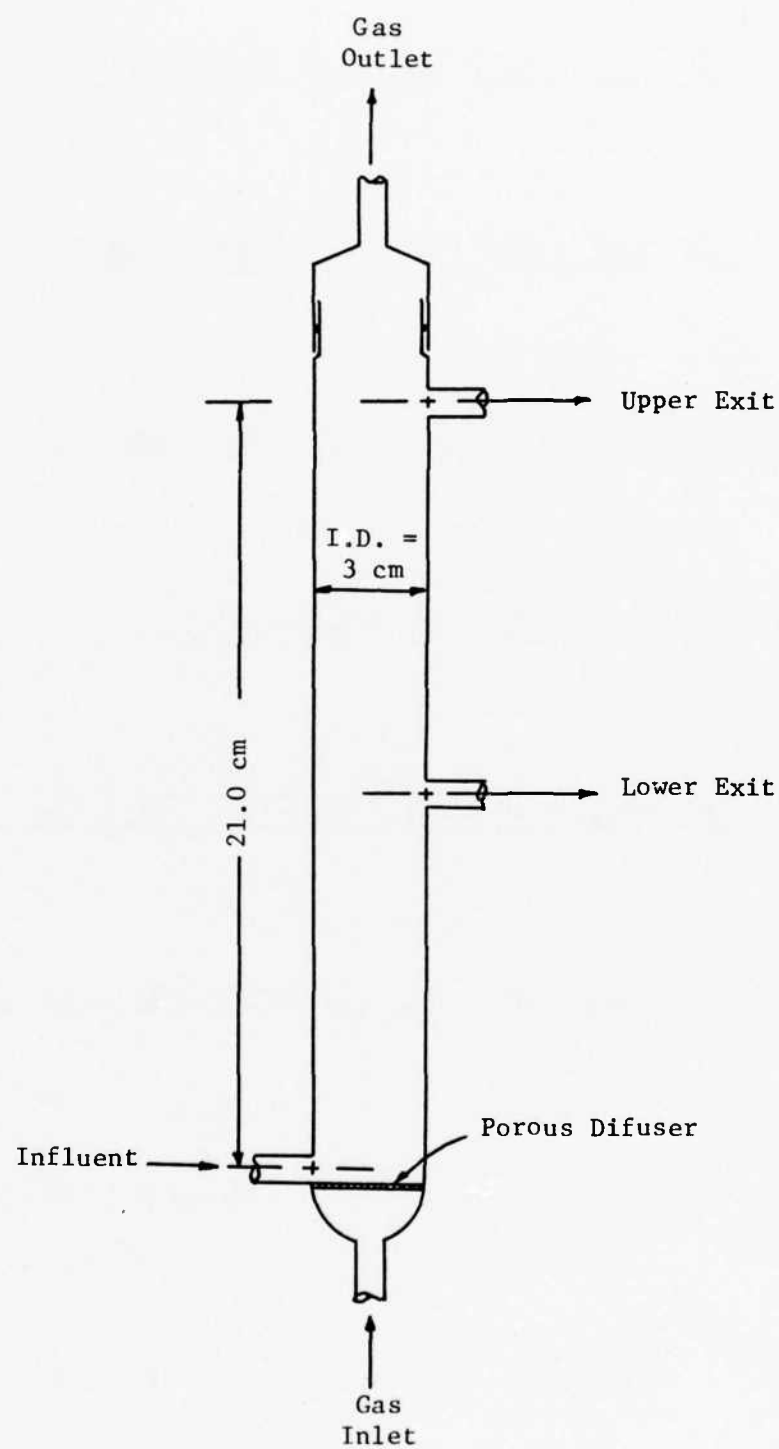


Figure 9. Dimension of the continuously flow reactor

had been filled initially with clear water. During the tracer study, the ozone-flow rate was the same as that used in ozone disinfection studies (200 ml/min) and the liquid volume was maintained at 160 ml. This resulted in a hydraulic detention time of 10 seconds. The dye concentration in the effluent was measured colorimetrically (603 nm, Beckman-26, UV-VIS-IR) and compared with the theoretical color concentration which can be predicted by the following equation:

$$\frac{C_e}{C_o} = 1 - e^{-t/d}$$

where C_e is the concentration in the reactor (or in the effluent), C_o is the concentration in the influent feed, d is the detention time, and t is the time after initiating the inflow. The experimental value of C_e/C_o was determined to be 0.644 as compared to a theoretically calculated value of 0.632 at t equals to the hydraulic detention time.

2. Effect of SAA on Ozone Disinfection in a Continuous System

Initial results obtained with samples collected from the overflow port of the reactor were rather scattered. This was due to inhomogeneity of the samples collected, i.e., the presence of foams along with the liquid samples. A more homogeneous sample was later obtained by sampling below the surface of water and foam. Results of experiments using the latter sampling techniques are shown in Table 3. It is seen from Table 3 that the survival of microorganisms in the absence of surfactant is always higher than that with the surfactant addition. Control experiments were run in the previous studies to show that there were no effects on cell enumeration with or without surfactant addition at a level of 3 ppm.

Table 3
The Effect of Surfactants on Ozone Disinfection

<u>Cationic SAA Dosage (ppm)</u>	<u>Residual Ozone, ppm</u>	<u>E. coli Survival #/100 ml</u>	<u>E. coli Survival** Percentage</u>	<u>Survival w/o SAA Survival w/SAA</u>
0	2.16	6.0×10^5	6.0×10^{-3}	-
1	1.62	4.2×10^5	4.2×10^{-3}	1.43
2	2.31	1.1×10^5	1.1×10^{-3}	5.45
3	2.08	2.4×10^5	2.4×10^{-3}	2.50

*Cetyltrimethylammonium bromide

** E. coli survival percentage = $\frac{\text{E. coli Survival (\#/100 ml)}}{\text{E. coli in Feed Reservoir (\#/100 ml)}}$

The E. coli concentration in the reservoir of feed solution was approximately $10^8/100 \text{ ml}$

More than five-fold decrease in the survival of fecal coliform was obtained with 2 ppm of a cationic detergent cetyltrimethyl ammonium bromide. The residual ozone concentrations were comparable to each other (Table 3) indicating the sole effect of detergent addition on cell survival. However, the residual ozone measurement was subject to errors due to the presence of a small amount of ozone bubbles trapped in the samples while collecting samples with the pipette. Refinement of ozone residual measurement using the technique of pipetting samples immediately underneath the water surface is thus necessary. This confirms the preliminary results (Phase I study) which showed a three-fold decrease in cell survival with the addition of 3 ppm of nonionic surfactant Brij 35. Results of these studies were quite encouraging in that they showed strong support to the theory proposed by Rosen (1974) and later confirmed experimentally by Farooq, Chian and Engelbrecht (1977).

C. Phase III Evaluation of Various SAA and Their Addition in Wastewater Effluent

The major efforts of this phase of study have been focused on the evaluation of different surface active agents in a clean system and verification of the effect of surface active agent addition on ozone disinfection in wastewaters.

1. Design of Ozone Contacting Systems

An improved continuously-flow reactor was fabricated in order to achieve a better mixing condition in the reactor. Figure 10 shows a schematic diagram of this system. The reactor employed in this study was made of Pyrex. It has an internal diameter of 6.0 cm and a height of 14 cm (Figure 11). Ozone gas was introduced at the bottom of the reactor through a fritted glass diffuser. Influent of inoculated water was fed into the reactor at the top through a

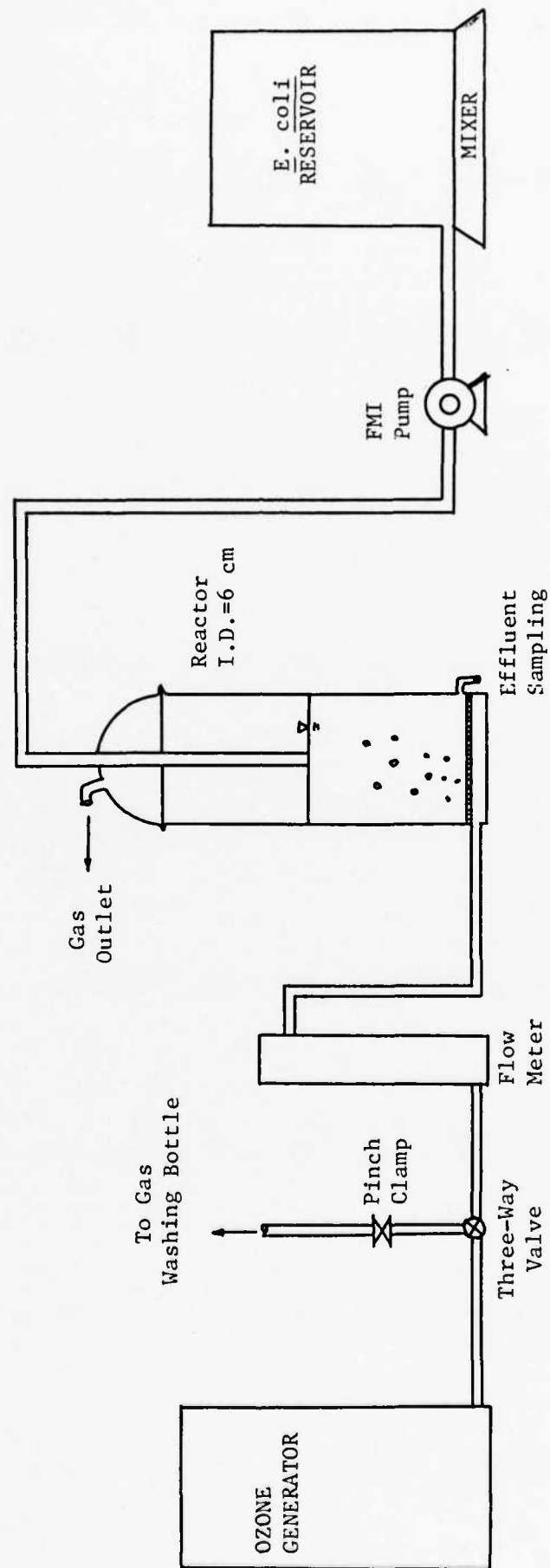


Figure 10. Schematic Diagram of a modified completely-mixed continuously-flow ozone disinfection system

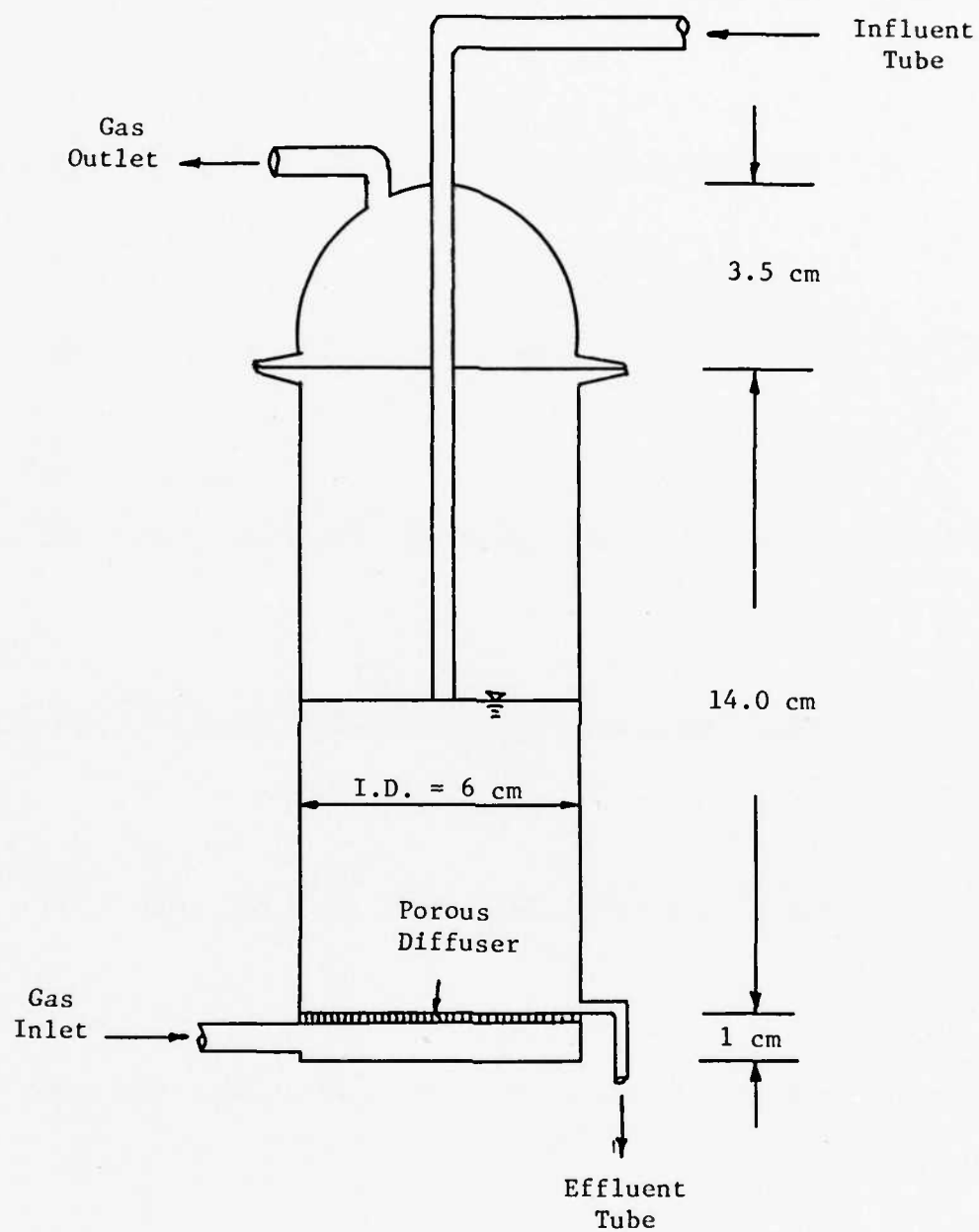


Figure 11. Details of the modified continuously-flow ozone contactor

glass tube. The exit of the influent tube rests immediately above the water surface in the reactor. The effluent was withdrawn from the bottom of the reactor. Neither foam nor ozone bubbles were found to be trapped in the effluent.

In order to assess the condition of mixing of the inoculated microorganisms in the reactor under the prevailing ozonation conditions, tracer studies were performed. Several different flowrates were examined for conditions of mixing. The influent feed rate to attain a best mixing condition was found to be 685 ml/min. The equivalent liquid volume to attain a hydraulic detention time of 20 seconds was approximately 230 ml. During the tracer study, the air flow rate was 200 ml/min which gives a VVM (volume of gas/volume of liquid/minutes) of 0.95. The dye concentration in the effluent was compared with the predicted concentration using the following equation:

$$\frac{C_e}{C_o} = 1 - e^{-t/d}$$

C_e = concentration in the reactor (or in the effluent)

C_o = concentration in the influent feed

d = detention time

t = time after initiating the inflow

The experimental values of C_e/C_o were plotted in Figure 12 along with the theoretical values as shown by the open circles. It is seen in this figure that a well-mixed flow condition is achieved in this reactor.

2. Effect of Different Surface Active Agents (SAA) on Ozone Disinfection

Three types of surface active agents were obtained. Two from each type were examined in this study as given in the following:

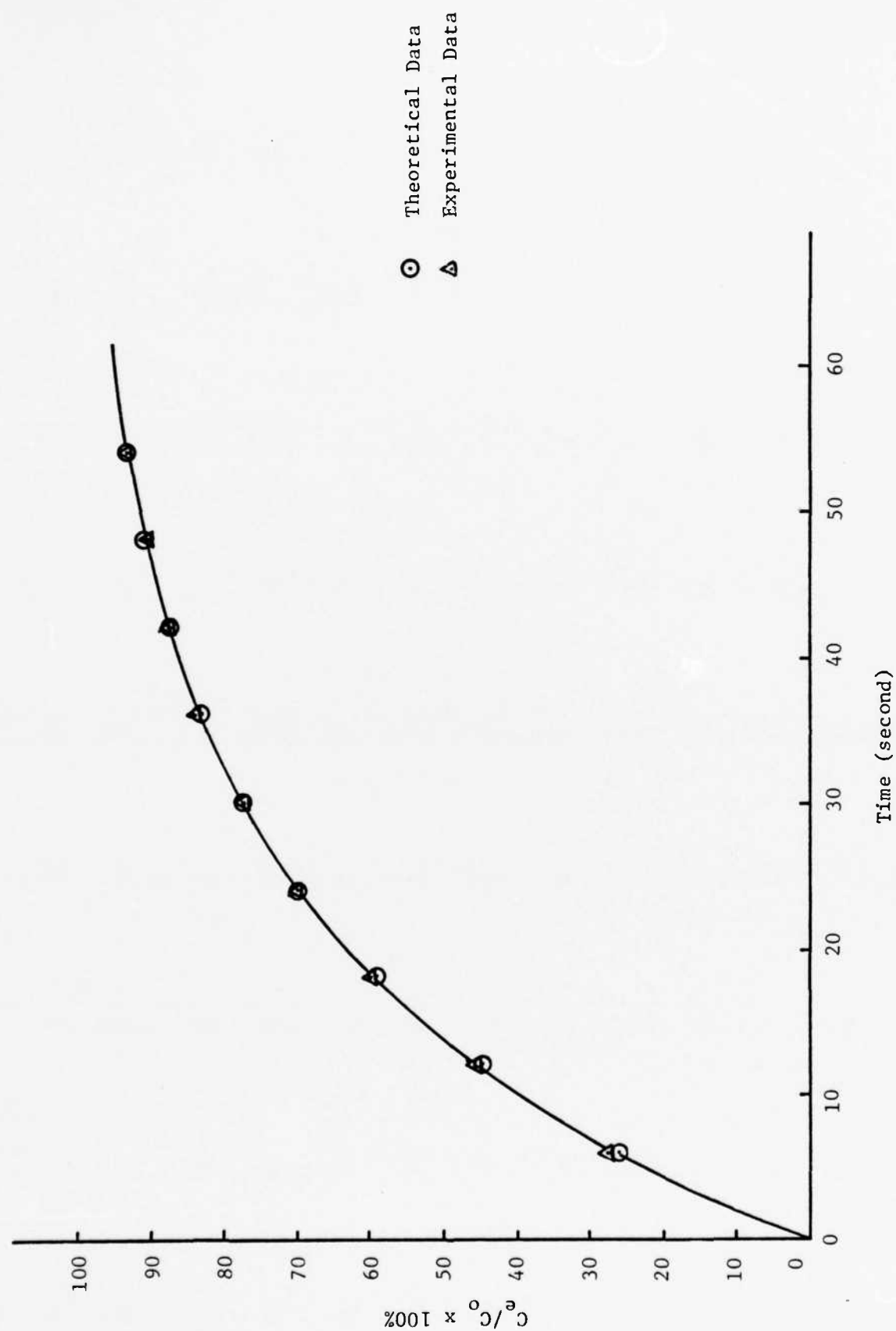


Figure 12. Tracer studies for mixing conditions in the ozone contactor

Anionic Surface Active Agent:
 Alkanol 189-S, DuPont (Sodium hydrocarbon sulfonate)
 Alkanol DW, DuPont (Sodium alkylarylsulfonate)
 Nonionic Surface Active Agent:
 Triton X-405, Rohm & Haas (Polyethoxy ethanol)
 Merpol LF-H, DuPont (Polyether)
 Cationic Surface Active Agent:
 Avitex LN, DuPont (Complex higher alkylamine composition)
 Zonyl FDC, DuPont (Fluorosurfactant)

The criteria used for the selection of surface active agents were based on the following properties:

Foaming condition
 Ozone concentration in the aqueous phase
 Inactivation of E. coli at the corresponding residual ozone concentrations

These properties were evaluated at a surface active agent concentration of 3 ppm, same as that used in the previous studies. The results are shown in the following:

a. Foam Testing of SAA

Objective: To examine the foaming conditions (which may cause enumeration error by foam concentration) and foaming problems associated with the treatment processes.

- Procedures:
- i. Run tap water at a flowrate of 685 ml/min with 3 ppm of SAA to the reactor. The liquid volume of the reactor was 230 ml. A hydraulic detention time was maintained at 20 seconds.
 - ii. Bubble with air through the bottom of the reactor. The flowrate of air was 0.2 l/min which yielded a VVM of 0.95.
 - iii. Observe the height of foaming after aerating for 1 min., i.e., 3 detention time.

Results:	<u>SAA</u>	<u>Type</u>	<u>Foaming Height (cm)</u>
	Alkanol 189-S	Anionic	No Foam
	Alkanol DW	Anionic	1.0-2.0
	Triton X-405	Nonionic	0.2-0.5
	Merpol LF-H	Nonionic	0.5-1.0
	Avitex LN	Cationic	1.0-1.5
	Zonyl FSC	Cationic	No Foam

Conclusion: Based on the foaming property, it showed that Alkanol 189-S, Zonyl FSC and/or Triton X-405 pose the least foaming problems.

b. The effect of SAA on the dissolved ozone concentration.

Objective: To examine the differences in dissolved ozone concentrations with different SAAs.

- Procedures:
- i. Pump tap water at a rate of 685 ml/min. A 3 ppm SAA was pre-mixed with the tap water. The liquid volume in the reactor was 230 ml. The hydraulic detention time was 20 seconds.
 - ii. Pass ozone gas through the bottom of the reactor. The gas flowrate was 200 ml/min. The ozone gas was generated from air through a Welsbach 816 ozonator at 70 V. and 8 psig. The ozone concentration in the gas phase was 32 mg/l.
 - iii. Collect the sample at the effluent after three detention time. The ozone concentration was then measured by spectrophotometric method using a Beckman 26 at 352 nm.

Results: Results of the above studies are given in Table 4.

Discussion: Except for Zonyl FSC, the dissolved ozone concentration found with other SAAs were around 2 mg/l (see Table 4). The use of Zonyl FSC gives the lowest value for the dissolved ozone, i.e., 1.5 mg/l. Therefore, based on a material balance, the ozone concentration in the gas phase with Zonyl FSC addition to the aqueous phase should be the highest. This phenomenon is quite significant in that the E. coli will then be exposed to a higher concentration of ozone in the gas phase. This would result in an enhanced inactivation of E. coli based on the bubble theory developed by Farooq, Chian and Engelbrecht (1977).

c. The effect of SAA on E. coli inactivation and ozone residue concentration in a clean system

Objective: To examine the effect of inactivation of E. coli upon addition of SAA and to determine the ozone residue after ozone disinfection.

- Procedures:
- i. Pump inoculated tap water at a flow rate of 685 ml/min. 3 ppm of SAA was added. The liquid volume was 230 ml. The detention time was 20 seconds.

Table 4

Effect of SAA Additions on Dissolved Ozone Concentrations

SAA	[O ₃]liq mg/l			Mean	Std. Dev.	% Std. Dev.
	#1	#2	#3			
Alkanol 189-S	2.00	1.98	2.05	2.01	0.029	1.4
Alkanol DW	2.10	2.09	2.10	2.10	0.005	0.2
Triton X-405	2.15	2.25	2.25	2.22	0.047	2.1
Merpol LF-H	2.00	2.15	2.14	2.10	0.068	3.2
Avitex LN	2.20	2.00	2.14	2.11	0.084	4.0
Zonyl FSC	1.55	1.50	1.35	1.47	0.085	5.8

- ii. Pass ozone gas through the bottom of the reactor at a flowrate of 200 ml/min. The ozone gas was generated from air through a Welsbach 816 ozonator at 50 V, 8 psig, and a total air flow rate of 2.0 l/min. The ozone concentration in the gas phase was 1.8 mg/l.
- iii. Collect the sample after 3 detention time and enumerate E. coli by plate count. Determine ozone residue concentration by using a Beckman 26 at 352 nm.

Results: The results of these experiments are given in Tables 5 and 6.

Conclusions: The results given in the above tables show that the degree of inactivation of E. coli follows the order of cationic SAA, nonionic SAA, and anionic SAA. The best result was obtained with the cationic Zonyl FSC which gives a nine- fold decrease in the survival of fecal coliform. This decrease was shown to be not caused alone by Zonyl FSC addition. The low ozone concentration found in this bulk liquid with Zonyl FSC addition suggests that the disinfection process occurred mainly at the gas-liquid interface. This confirms with the bubble theory developed by Farooq, Chian and Engelbrecht (1977).

Table 5

The Effect of SAA Additions on Inactivation of E. coli and Ozone Residuals

SAA	Residual Ozone ppm	<u>E. coli</u> Initial #/100 ml	<u>E. coli</u> Survival #/100 ml	<u>E. coli</u> Survival Percentage	Survival of Control with SAA
Control (no SAA)	1.10	10^8	1.4×10^2	1.4×10^{-6}	-
Alkanol 189-5	0.98	10^8	0.37×10^2	0.37×10^{-6}	3.8
Alkanol DW	-	-	-	-	-
Triton x-405	1.09	10^8	0.23×10^2	0.23×10^{-6}	6.1
Merpel LF-H	-	-	-	-	-
Avitex LN	-	-	-	-	-
Zonyl	0.88	10^8	0.15×10^2	0.15×10^{-6}	9.3*

* Due to the excellent results obtained with Zonyl FSC addition, an additional control run was made by adding 3ppm of Zonyl FSC to the inoculated tap water in activation of E. coli by passing only air through the inoculated tap water in the presence of Zonyl FSC. Results showed that the count for E. coli reduced from $10^8/100$ to $0.7 \times 10^8/100\text{ml}$ which was not significant while compared to a nine-fold decrease in the survival of E. coli in presence of ozone.

Table 6
The Effect of Other SAA
Inactivation of E. coli at a Higher Concentration

<u>SAA</u>	<u>Residual Ozone ppm</u>	<u>E. coli Initial #/100ml</u>	<u>E. coli Survival #/100ml</u>	<u>E.coli Survival Percentage</u>	<u>Survival of Control with SAA</u>
Control (No SAA)	0.88	6×10^9	6×10^4	1×10^{-5}	-
Alkanol DW	1.14	6×10^9	4.4×10^4	0.73×10^{-5}	1.37
Alkanol 189-5	0.97	6×10^9	3.8×10^4	0.63×10^{-5}	1.59
Merpol LF-H	1.08	6×10^9	3.6×10^4	0.6×10^{-5}	1.67
Avitex LN	1.08	6×10^9	3.4×10^4	0.57×10^{-5}	1.75

3. Determination of Surfactants in Wastewater

While evaluating SAA addition on ozone inactivation of microorganisms in wastewater, it was necessary to determine the amount of synthetic detergents already present in wastewater so that the net effect of SAA addition can be fully assessed. The methylene blue method for methylene-blue active substances as described in Standard Methods (1975) was used. The standard solutions of a linear alkylated sulfonate (LAS) were prepared to calibrate the amount of synthetic detergents in wastewater. Table 7 gives the results of calibration runs. The percentage standard deviation is less than 10% at low concentration range and less than 1% at high concentration range.

Wastewater samples obtained from three separate days were analyzed for their LAS content using the methylene blue method. The results of analysis are shown in Table 8. A range from 0.1 to 0.5 ppm of LAS equivalent materials was found in these wastewater samples. The reproducibility of the analytical procedure is excellent. The percentage standard deviation obtained with triplicate samples is approximately 2% (Table 8). Although the amount of surfactants (mainly anionic) found in these wastewater samples was lower than the level of SAA addition (i.e., 3 ppm) evaluated with the clean water samples; it should be noted, however, that the results of analysis reflect only the methylene blue active materials. The actual level of detergents in wastewater may be higher if surfactants other than the anionic ones are present. This may render the effect of SAA addition to wastewater on ozone inactivation of microorganic somewhat less effective than that observed with the clean water system.

4. Effect of SAA Addition to Wastewater on Ozone Inactivation

The procedures employed in this study were similar to those described under section 2c of Phase III study. An addition of 3 ppm of Brij 35 in wastewater samples was evaluated. The results of these experiments are given in Table 9. Since the secondary effluents obtained in this study contained a level of E. coli ranging from 2×10^8 to 4×10^{10} per 100 ml, no inoculation was necessary. In experiment 1, the wastewater sample was diluted 400 fold in order to adjust the amount of E. coli to 10^8 /100 ml range. The control sample refers to no SAA addition. The detention time employed in these continuous runs were 20 seconds. After a few volume turnovers, the steady-state concentrations of E. coli in both the control and the test samples (with 3 ppm Brij 35 addition) were literally zero. The residual ozone concentrations were found to be 0.30 and 0.28 ppm respectively in the control and the test samples. At such levels of residual ozone concentrations, ozone inactivation of E. coli is expected to be complete within a period of 20 seconds (Farooq, 1976).

In experiments 2 and 3 undiluted wastewaters obtained from different days were tested. The results of these runs show some improvement in ozone inactivation, i.e., ranging from 20 to 53%. These values are, however, significant as compared to the variation encountered in cell enumeration procedures which were found to be less than 20% from the average. The smaller effect of SAA addition to wastewater on ozone inactivation as compared to a clean system is expected in that there were already detergents present in the wastewater effluent (see Section 3c). A decrease in both COD and total suspended solids was also observed during all ozone disinfection runs. Whether these decreases were due to foam separation remains to be determined.

D. Phase IV Ozone Disinfection with the Aid of Motionless Mixers

The purpose of these experiments was to utilize the high gas-liquid interfacial areas generated with the use of different motionless mixers. A variety of motionless (static) mixer devices capable of generating turbulent flow in a tubular reactor has been reviewed. These included tubes containing meshes, Kenics mixers, Sulzer mixers, Etoflo mixers, Lightnin mixers, Koch mixers, or a throttling valve (see Appendix II for literature review). Of all these devices, the Lightnin and Koch mixers appear to give the most versatility in terms of changes in in-line configuration of the mixer elements. A 1" diameter by 16" long Lightnin in-line mixer and 5 1" diameter by 1" long Koch mixer elements were obtained in this study.

1. Design of Ozone Contactor Incorporating Motionless Mixers

The finalized design and fabrication of an ozone contacting system using a Koch or Lightnin in-line mixer is given in Figure 13. The reactor was made of Plexiglas. It has an internal diameter of 4 in. and a designed liquid height between 8.5 in. and 9.5 in. (the liquid height can be adjusted by means of an adjustable screwed-on tubular weir). A cone-shaped damper was located at the bottom of the reactor which is directly above the inlet from the in-line mixer in order to evenly distribute the incoming flow and minimize dead zones around the bottom (Figure 14).

2. Preliminary Studies on Ozone Disinfection with Contactor Incorporating Motionless Mixers

The ozone contactor system was operated by recirculating at a flowrate of 15 liters/min through the 1" in-line mixer in order to generate a turbulent flow condition (Reynolds number was approximately 1.5×10^4). The wastewater was fed at a flowrate of 1 liter/min through

the port approximately 2 inches below the in-line mixer column. The hydraulic detention was 9 seconds within the reactor system. Ozone gas was introduced through the port located approximately 1" below the in-line mixer at a flowrate ranging from 0.2 to 1.0 liter/min. The ozone gas was generated from air cylinder through a Welsbach 816 ozonator operated at 70 and 8 psig. The gas phase ozone concentration was 1.98 mg/l. Samples were collected after 3 detention time (i.e., after 27 seconds). The survival of E. coli, ozone residuals, COD and total suspended solids were then determined.

Preliminary results showed that a two log-cycle reduction of E. coli was observed at a ozone gas flowrate of 1.0 liter/min. This is substantially lower than the four to five log-cycle reduction of E. coli obtained with a continuously flow ozone sparged system operated at a detention time of 20 seconds (Table 9). A 3 log-cycle reduction of E. coli was observed with the in-line mixer system fed with wastewater effluents passing through an activated carbon (Filbrasorb 300) operated at a flowrate of 5 gpm/ft². The reasons for the low efficiencies of ozone inactivation with the use of the ozone contacting system incorporating in-line mixers are still under investigation. These could be due to the shorter detention time (i.e., 9 seconds) employed in these experiments as compared to 20 seconds employed in previous experiments with a continuously flow reactor. Poor mixing condition encountered in the contactor vessel (Figure 14) may also result in low efficiency of ozone disinfection due to short circuiting.

Table 7

Standard LAS Solution vs Absorbance

LAS* (ml)	<u>Absorbance (625 nm)</u>			Mean	Standard Deviation	% Standard Deviation
	#1	#2	#3			
0	0.013	0.025	0.036	0.025	9.4×10^{-3}	37.6
1	0.078	0.088	0.096	0.087	7.4×10^{-3}	8.5
3	0.119	0.130	0.105	0.118	1.0×10^{-2}	8.5
5	0.216	0.225	0.225	0.222	3.7×10^{-3}	1.7
10	0.301	0.317	0.317	0.312	7.5×10^{-3}	2.4
20	0.541	0.537	0.539	0.539	1.6×10^{-3}	0.3
30	0.714	0.707	0.711	0.711	2.9×10^{-3}	0.4
40	1.046	1.043	1.042	1.044	1.7×10^{-3}	0.2

Note: *: 1 ml of Standard LAS = 10 mg LAS.

Table 8

LAS Concentration in Wastewater

Sample	Absorb- ance	LAS* conc. (mg/l)	Mean	Standard Deviation	% Standard Deviation
1	0.340	0.480	0.492	8.6×10^{-3}	1.7
	0.350	0.500			
	0.348	0.496			
2	0.104	0.084	0.082	1.6×10^{-3}	2.0
	0.100	0.080			
	0.103	0.082			
3	0.316	0.440	0.453	9.4×10^{-3}	2.1
	0.323	0.460			
	0.323	0.460			

Note: *LAS concentration (mg/l) = mg/sample size in liter.
As in this test the sample size was 250 ml.

Table 9

The effect of SAA Addition on Inactivation of E. Coli
and ozone residuals in Secondary Effluent

Experiment	Residual Ozone (ppm)	<u>E. Coli</u> Initial #/100 ml	<u>E. Coli</u> Survival #/100 ml	<u>E. Coli</u> Survival Percentage	Survival of control with SAA
#1 Control*	0.30	10^8	0	0	-
#1*	0.28	10^8	0	0	-
#2 Control	~ 0	1.6×10^{10}	4.2×10^5	2.6×10^{-5}	-
#2	~ 0	1.6×10^{10}	3.5×10^5	2.2×10^{-5}	1.2
#3 Control	~ 0	2.0×10^8	2.9×10^4	1.45×10^{-4}	-
#3	~ 0	2.0×10^8	1.9×10^4	0.95×10^{-4}	1.53

Note: *5 ml of secondary effluent was diluted with 2 liters of tap water which lowers the E. Coli in the original secondary effluent of $4.0 \times 10^{10}/100$ ml down to $10^8/100$ ml.

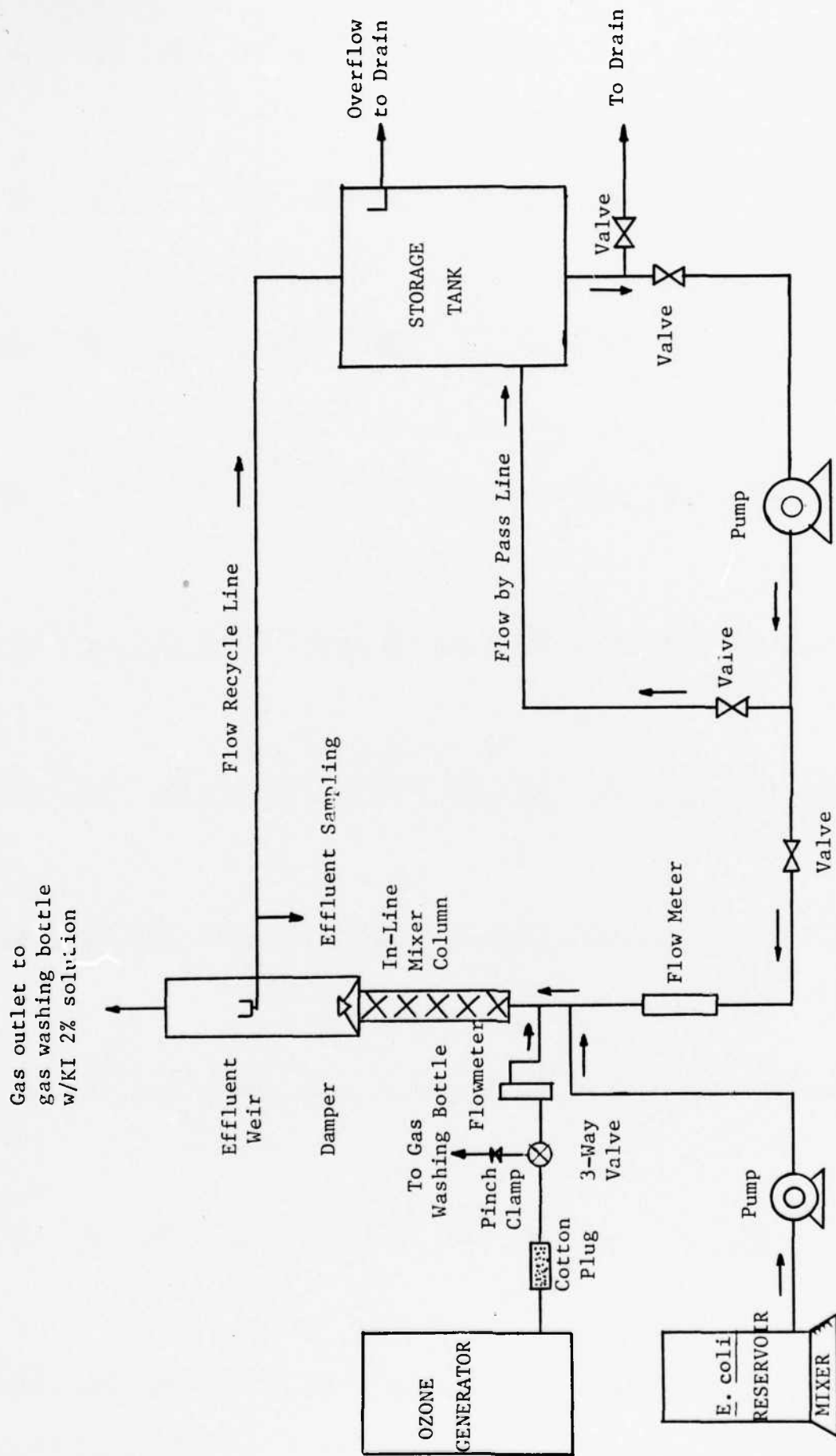


Figure 13. Finalized design of an ozone contacting system incorporating a Lightnin in-line mixer

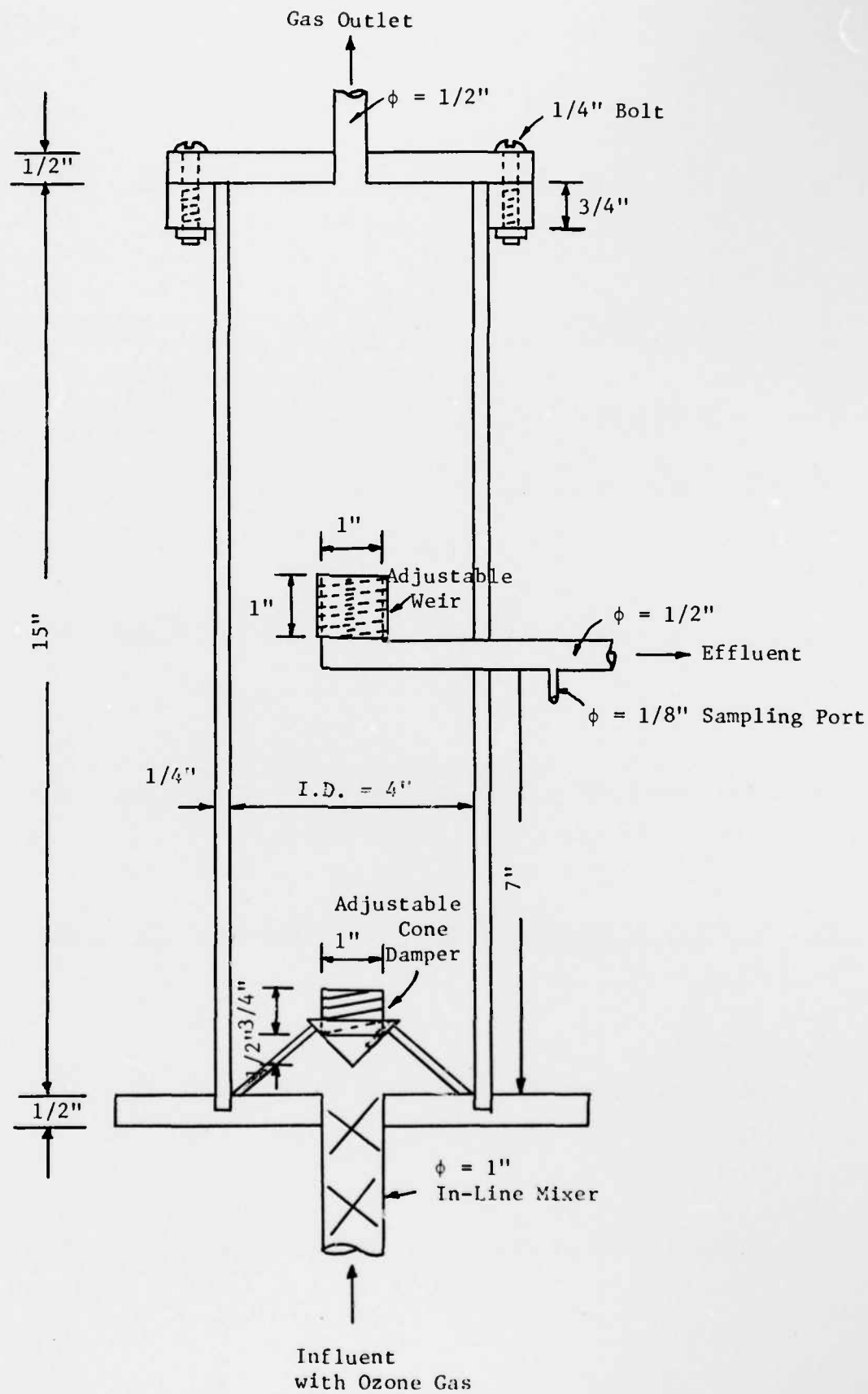


Figure 14. Details of an ozone contactor in conjunction with an in-line mixer

CONCLUSIONS

Up to a one log-cycle improvement in ozone inactivation of E. coli was observed with the addition of 3 ppm of surface active agents in a clean water system. The most effective surface active agent was found to be a cationic detergent, Zonyl FSC, manufactured by Dupont. The use of Zonyl FSC, a fluorosurfactant, resulted in a ten-fold increase in inactivation at a 30% decrease in residual ozone concentration in clean water. Results of this study further supported the concept that ozone inactivation occurs at gas-liquid interphase rather in the bulk.

The effect of surface active agent addition on ozone disinfection was confirmed with the use of a secondary effluent. The effect of enhanced inactivation was, however, not as distinct as that obtained with a clean water system. This was due to the presence in wastewater effluent of a small amount of anionic detergent to begin with. This tended to reduce the relative effect of surface active agents addition on ozone disinfection of a wastewater effluent.

Preliminary results obtained with a mechanical system employing Lightnin and Koch motionless mixers showed that the mechanical systems were not as efficient as the ozone sparged vessel in ozone disinfection of wastewater with or without surface active agent addition. A ten-fold increase in ozone disinfection was observed by using activated carbon treated secondary effluent with the motionless mixer system. An analysis of the motionless mixer system revealed that both the hydraulic detention time and the ozone dosage were lower as compared to that employed in a sparged vessel. In addition, the complete mixing in the holding vessel of the motionless mixer system was not attained. Future work will be carried out to compare a sparged vessel vs a motionless mixer system under identical operating conditions.

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APPENDIX I

Surface Active Agent

A surface-active agent (or, more briefly, surfactant) is a substance that, when present at low concentrations in a system, has the property of adsorbing onto the surfaces or interfaces of the system and of altering to a marked degree of the surface or interfacial free energies of those surfaces (or interfaces). The term "interface" indicates a boundary between any two immiscible phases; the term "surface" denotes an interface where one phase is a gas, usually air.

The interfacial free energy is the minimum amount of work required to create that interface. The interfacial free energy per unit area is what we measure when we determine the interfacial tension between two phases. It is the minimum amount of work required to create unit area of the interface or to expand it by unit area. When we measure the surface tension of a liquid, we are measuring the interfacial free energy per unit area of the boundary between the liquid and the air above it. When we expand an interface, therefore, the minimum work required to create the additional amount of that interface is the product of the interfacial tension times the increase in area of the interface. A surface-active agent is therefore a substance that at low concentrations adsorbs at some or all of the interfaces in the system and significantly changes the amount of work required to expand those interfaces. Surfactants usually act to reduce interfacial free energy rather than to increase it, although there are occasions when they are used to increase it.

Surface-active agents have a characteristic molecular structure consisting of a structural group that has very little attraction for the solvent water, known as a lyophobic (hydrophobic) group, together with a group that has strong attraction for the solvent, called the lyophilic (hydrophilic)

group. This is known as an amphipathic structure. Because of the presence of the lyophilic group a surfactant is more or less readily soluble in water. However, the lyophobic group is repelled by water, so that there is a tendency for that portion of the molecule to leave the aqueous phase. This leads to a higher concentration at the surfaces or boundaries than in the main body of the solution. At the surface of the solution - the air-water interface - the surfactant molecules orient themselves with the lyophilic groups in the water phase, the lyophobic groups extending as far as possible in the other direction, still consistent with the molecular dimensions and geometry and with the intermolecular forces acting upon them. The result of this oriented surface film is the lowering of the surface tension of the water, and a greater tendency toward bubble and foam formation. In the presence of an immiscible liquid, a similar layer tends to form at the liquid-liquid interface, lyophilic groups oriented toward the water, lyophobic toward the other liquid. This promotes dispersion and emulsification as droplets. At liquid-liquid interfaces, a similar phenomenon occurs.

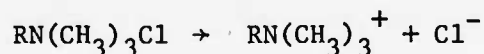
Another phenomenon characteristic of surfactants in aqueous solution is the aggregation of their molecules into larger, oriented groups called micelles. In very dilute solutions, say 1 ppm, the individual single molecules are present, or their ions. Further increments of surfactants also dissolve to form separate molecules or ions up to a certain point, known as the critical micelle concentration. In the micelles of an aqueous solution, the molecules are oriented with their lyophobic portions clustered together, the lyophilic ends extending outward. Many organic materials which are insoluble in water but soluble in organic solvents may be solubilized in aqueous solution to a certain extent by the presence of surfactant micelles. The organic material is found to be molecularly dispersed in the internal region of the micelle as a quasi-solution in the clustered lyophobes, one or more (or less) molecules per micelle.

The general properties of surfactants outlined above stem from their general structures - molecules in which a lyophilic group is linked to a lyophobic group. The lyophobic groups, lyophilic groups and the modes of linking them together may be combined to give surfactants in unlimited variety. The size of such compendia as Schwartz and Perry (1949, 1958), Linfield (1976), Jungermann (1970), and Schick (1967) attest the diligence with which the permutations and combinations of these have been explored since the 1920s.

The lyophobic group is usually a long-chain hydrocarbon residue, less often a halogenated or oxygenated hydrocarbon or siloxane chain; the lyophilic group is an ionic or highly polar group. Depending on the nature of the lyophilic group. Surfactants are classified as:

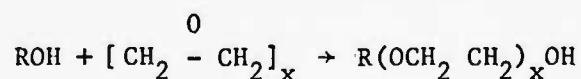
1. Anionic - surfactants are those which give negatively charged surfactant ions in aqueous solution, usually originating in sulfonate, sulfate, or carboxylate groups, for example, $\text{RSO}_3\text{Na} \rightarrow \text{RSO}_3^- + \text{Na}^+$. Commercially, these are very important and represent the major fraction of surfactants in use today. For the most part they are produced by sulfonation or sulfation of the desired lyophobes.

2. Cationic - surfactants are those which give a positively charged surfactant ion in aqueous solution, for example,



These are of interest in the detergent industry principally because of their bacteriostatic or germicidal properties.

3. Nonionic - surfactants contain lyophilic groups which do not ionize appreciably in aqueous solution. The ones of greatest commercial importance contain a polyether lyophobe group derived from ethylene oxide., for example,



Differences in the nature of the lyophobic groups are usually less pronounced than in the nature of the lyophilic group. Generally, they are long-chain hydrocarbon residues. However, they include such different structures as:

1. Straight-chain, long alkyl groups ($C_8 - C_{20}$).
2. Branched-chain, long alkyl groups ($C_8 - C_{20}$).
3. Long-chain ($C_8 - C_{15}$) alkylbenzene residues.
4. Alkyl-naphthalene residues (C_3 and greater-length alkyl groups).
5. Rosin derivatives.
6. High molecular-weight propylene oxide polymers (polyoxypropylene glycol derivatives).
7. Long-chain perfluoroalkyl groups.
8. Polysiloxane groups.

Products are also in use which do not fit precisely into one of the three main categories, anionic, cationic, or nonionic, or which belong to more than one. These have been designed with a variety of special properties for specialty uses and thus will be not discussed here.

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APPENDIX II

Motionless Mixer

Motionless mixing is a relatively new concept in mixing that was developed in the early 1960's. It has been gaining use over the conventional methods, such as batch mixing in large tanks. These motionless mixing devices are quite simple and are designed to provide regular division and recombination of the fluid via vanes or channel systems introduced into the flow path. These mixers can be divided into five types:

1. Altering 180 degree helixes
2. Altering 270 degrees helixes
3. Semi-elliptical baffles
4. Corrugated panels
5. Directed channels

Table 1 lists the various commercial motionless mixers according to type.

Motionless mixers offer many advantages. They provide a much more uniform shear pattern than dynamic mixers. When considering the energy cost for a blending operation, the motionless mixer is competitive with other methods, and the cost relationship becomes more favorable for motionless mixers as the viscosity increases (1,2). At high viscosity, power consumption for a motionless mixer can be less than half of that required for a comparable dynamic mixer. Motionless mixers also provide great versatility since they can cover a much broader range of viscosity (10^{-2} to 10^{12} centipoise) than that which is possible with any other type of mixing device.

Motionless mixers have been used in a wide variety of applications. They are used for both low and high viscosity blending operations, plug flow reactors, mass transfer devices, and dispersion devices for liquid-

TABLE 1

Commercially Available Motionless Mixers

<u>Mixer</u>	<u>Manufacturer</u>	<u>Mixer Type</u>
Kenics	Chemineer/Kenics	180° Helixes
LPD LLPD	Charles Ross & Son	Semi-elliptical
ISG	Charles Ross & Son	Directed Channels
Koch/Sulzer	Koch Engineering Co.	Corrugated Panels
Komax	Komax Systems	Semi-elliptical
Lightnin Inliner	Mixing Equipment Co.	180° Helixes
Koch/Sulzer BKM	Koch Engineering Co.	Semi-elliptical

liquid, gas-gas, and gas-liquid contacting (3,4,5,6,7). Yet to gain maximum benefits from motionless mixers, the flow pattern and the mixing performance should be studied.

In the past, hydrodynamic models were put forward by Middleman (8) for turbulent flows and by Hartung and Hiby (9) for laminar flow. A dispersion model approach was chosen by Chen et al. (10) and by Lai and Fan (11) and stochastic models were advanced by Chen et al. (12) and by Wang and Fan (13). Whilst models of turbulent flow may be used for any mixer, the laminar flow models are restricted to one type only. The analysis by Hartung and Hiby (9) is applicable to the Kenics mixer whilst a more recent analysis by Ulbrecht and Shintre (14) applies to Sulzer-Koch mixer.

Motionless mixers are basically flow channels regardless of the many convolutions, baffles and vanes that they introduce in the flow path. Analysis of pressure losses through the motionless mixer is certainly complicated by the variance from straight flow paths, wall roughness and other factors that affect any flow system. It is possible to extend the use of the Darcy or Fanning equation to the static mixers. The equation is:

$$\frac{\Delta P}{L} = \frac{Cf}{D} \frac{\rho V}{2g_c}$$

where C is a constant depends on the definition of the friction factor, f, and D is the hydraulic diameter, L is the length of mixer, and V is superficial velocity. Currently all manufacturers of motionless mixers use modified forms of the Darcy equation. Richardson (15) has summarized the results of typical pressure drop calculations for laminar and turbulent flow as shown in Table 2 and 3, respectively, for single phase system.

Multi-phase systems greatly complicate pressure drop calculations. Because of the complicated phenomena involved, these systems have been

TABLE 2

Comparison of Predicted Pressure Drop

Laminar Flow

Flow Rate = 56.8 liters/min.

Viscosity = 10 K centipoise

Specific Gravity = 0.9

Nominal Mixer Diameter = 3"

<u>Mixer</u>	<u>Equation to Predict Flow Divisions</u>	<u>Elements Required for 10⁶ Flow Divisions</u>	<u>Number of Flow Divisions</u>	<u>Pressure Drop (kPa)</u>
Kenics	FD = 2 ^N	20	1.05x10 ⁶	91.7 (Table)
		20	1.05x10 ⁶	150.3 (Equation)
Koch AY	FD = $\frac{(2M)^N}{2}$	6	1.49x10 ⁶	369.0
Komax	FD = 2 ^N	20	1.05x10 ⁶	150.3
Lightnin ¹	FD = 3*2 ^{N-1}	20	1.57x10 ⁶	184.1
Ross ISG LPD	FD = 4 ^N	10	1.05x10 ⁶	1724.1
	FD = 2 ^N	20	1.05x10 ⁶	160.7

¹ Elements here correspond to what Mixco has called flights. Their flight is made up of seven of their elements.

Variables:

N = Number of elements

M = Number layers of corrugation in Koch/Sulzer mixer

TABLE 3

Comparison of Predicted Pressure Drop

Turbulent Flow

Example:

Flow Rate = 946.3 liters/min.

Viscosity = 10 centipoise

Specific Gravity = 1.1

Nominal Mixer Diameter = 4"

<u>Mixer</u>	<u>Pressure Drop (kPa)</u>	
Kenics	38.6	(Table)
	43.4	(Equation)
Koch AY	82.8	
Komax	44.1	
Lightnin	86.2	(Turbulent Configuration)
Ross LPD	80.0	
ISC	1407.0	

handled by either assuming a pseudo-homogeneous system or by using an empirical two-phase correlation. Generally, the factors which decide which of the above mentioned methods to use are the ratios of the viscosities and densities; when ratio close to one, pseudo-homogeneous approach is used. While for large differences in this ratio, two-phase model is used. Dukler et al. (16), have proposed equations to calculate the pressure drop for pseudo-homogeneous and two-phase systems. The most widely used method for liquid-gas systems is the Lockhart-Martinelli correlation (17). It considers the frictional pressure drop of each phase as if it occupied the entire flow channel alone. The correlating parameter is

$$X = [(\partial P / \partial Z)_L / (\partial P / \partial Z)_G]^{0.5}$$

The two-phase pressure drop can then be calculated from:

$$(\frac{\partial P}{\partial Z})_{tp} = \phi_G^2 (\frac{\partial P}{\partial Z})_G = \phi_L^2 (\frac{\partial P}{\partial Z})_L$$

where ϕ_G and ϕ_L are empirical constants determined as a function of X.

Motionless mixers provide excellent dispersions of gaseous and liquid phases in a liquid stream when operated with a highly turbulent flow. Drop or bubble formation in a two-phase mixer is primarily a turbulence related process. Three forces are known to influence the formation of droplets. They are inertia force, interfacial tension and viscous force in the dispersed phase. The drop size has been studied by a lot of researchers. The studies were based on the dispersion model developed by Kolmogorov (18), and Hinze (19, 20). Middleman (21) has utilized the Kolmogorov-Hinze model in his work with Kenics mixers. He defines the Sauter mean drop diameter by the equation:

$$\frac{\bar{d}_{32}}{D} = C We^{-0.6} Re^{0.1}$$

where \bar{d}_{32} is the Sauter mean drop diameter and is defined as $\bar{d}_{32} = \frac{\sum n_i d_i^3}{\sum n_i d_i^2}$, D is the inside diameter of the mixer, C is a constant. We is the Weber number, and Re is the Reynolds number. Chen (1) has utilized empirical curves which plot (\bar{d}_{32}/D) against the Weber number in his predictions of Kenics mixer performance. Arbo and Barbini (21) followed Middleman's analysis in their work with Ross LPD and LLPD mixers, but they neglect the Reynolds number term ($Re^{0.1}$). Strieff (22) neglect the turbulence theory completely and relied on an analysis of viscous drag in his work with the Koch mixers, the resulting equation is

$$\frac{\bar{d}_{32}}{D} = 0.21 We^{-0.5} Re^{0.15}$$

which looks quite similar to the equations from turbulence theory.

The results of these predictions are given in Table 4. Since the motionless mixers provide a more uniform shear field, Middleman (8) has reported that coalescence can be neglected in them except at very low Weber number ($We < 12$).

Bubble size predictions for liquid-gas systems should also be correlated by the same turbulence theory. Chen and Libby (23) in their work with Kenics worked out the correlation between air and water as:

$$\frac{\bar{d}_{32}}{D} = 0.39 We^{-0.43}$$

Middleton (24) also studied the performance of various inserts in tubes for gas-liquid mass transfer in turbulent flow. Measurements of mass transfer ($k_L a$) and gas hold-up for the air-water system in a variety of tubular devices, in turbulent flow, used both in vertical upflow and downflow configurations were given in his report. The inserts include meshes, Kenics mixers, Sulzer mixers, Etoflo mixers, and a throttling valve.

TABLE 4

Drop Size Predictions

<u>Mixer Type</u>	<u>Length (cm)</u>	<u>Sauter Mean Drop Size (μm)</u>	<u>Pressure Drop (kPa)</u>
5.3 cm Kenics	52.1	343	41.7 kPa
5.3 cm Koch BY	31.5	217	83.4 kPa
5.3 cm Ross LPD	45.7	446	64.1 kPa
5.3 cm Open Pipe ¹	106.0	1180	0.75 kPa
3.2 cm Helical Coil ² (5.3 cm helix diameter)	120.0	680	7.48 kPa

Kolmogorov length in open pipe = 33 μm

Maximum applicable drop diameter³ = 3200 μm

1. Based on Kolmogorov-Hinze model at 200 pipe diameters
2. Using equivalent hydraulic radius to Kenics, flow adjusted to correct for area change
3. Not including Koch mixer

By applying motionless mixers, it is obvious that a more efficient blending and mixing is reached, but they demand accurate feed metering or the efficient blending is valueless, so in order to employ the motionless mixer in an optimal manner, it is important that accurate predictions of mixer performance should be made.

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